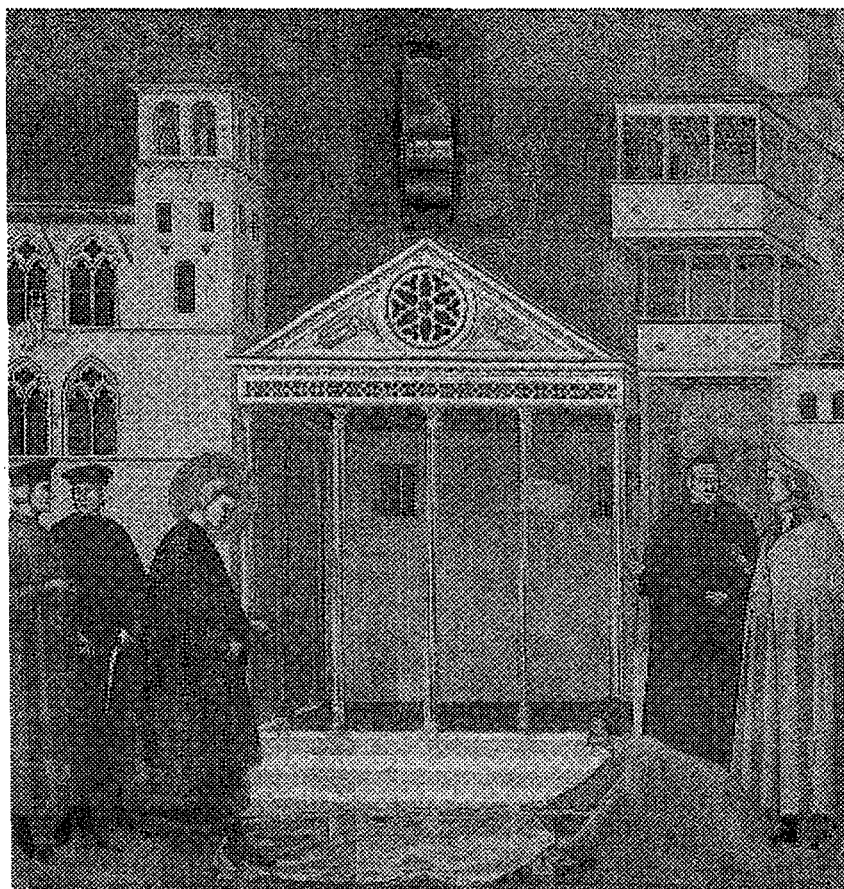# COMET XVI

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XVI INTERNATIONAL CONFERENCE ON MOLECULAR ENERGY TRANSFER

June 20-25, 1999
"La Cittadella"
ASSISI, Italy

BOOK OF ABSTRACTS

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The Final Proceedings for The 1999 Conference on Molecular Energy Transfer (COMET XVI), 20 June 1999 - 25 June 1999

This is an interdisciplinary conference that concerns energy transfer in nonequilibrium gases and liquids. Topics include the reaction dynamics of polyatomic systems and in photodissociation processes, energy transfer between chormophores, and energy transfer in reactive ion-neutral collisions.

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XVI International

Conference On Molecular Energy Transfer

COMET XVI

"La Cittadella"
ASSISI, Italy

June 20-25, 1999

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CONFERENCE PROGRAMME

AND

ABSTRACTS

COMET XVI

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Sponsors of COMET XVI Conference

We wish to thank the following for their contribution to the success of this conference:

- European Office of Aerospace Research and Development (EOARD), Air Force Office of Scientific Research (AFOSR), United States Air Force Research Laboratory (USAFRL).

- University of Perugia.

Caption of Front Cover:

FRANCIS HONORED BY A SIMPLE MAN: A citizen of Assisi spread his cloak on the ground before Francis who was still a youth. Thus he gave honor to Francis and asserted, under inspiration from God, that Francis was worthy of respect and reverence by all because he was going to accomplish great things.
This is the first episode (of twenty-eight) of the life of Francis, which Giotto and his school depicted between the years of 1296-1300 in The Upper Basilica of St. Francis.
The scene is set in the Main Square of Assisi, as it can also be seen today. The Temple of Minerva (which actually has six columns rather than five, as it was depicted by Giotto) is in the background.

Foreword

Continuing progress in the understanding of molecular energy transfer and of its importance has provided the impetus for a series of conferences on this topic, starting from 1969. These conferences have been held biannually, alternating as a Gordon Research Conference (GRC) on Molecular Energy Transfer and as a European Conference on Molecular Energy Transfer (COMET). The dates, sites, and organizers of previous and forthcoming GRC/COMET conferences in this series are listed on the following page. The University of Perugia is honored to host the sixteenth conference of the series, which is the first to be held in Italy.

Energy transfer plays a central role in nonequilibrium gases and liquids. Inelastic collisions provide the mechanism whereby internal (vibrational, rotational, and/or electronic) energy is transferred between molecules or lost into translational degrees of freedom. Nonequilibrium phenomena in combustion and in the atmosphere, collisional processes in the interstellar space, the pumping of lasers and masers are some examples of processes where molecular energy transfer is of key importance. Energy transfer plays also an important role in chemical reactions and in biological systems. Continuing experimental advances permit the study of the transfer of energy within molecules, between molecules, or between molecules and surfaces with higher and higher resolution as well as on shorter and shorter timescales. Ultimately, the efficiency of energy transfer and its selectivity are governed by inter- and intra-molecular forces. Theoretical advances, both methodological and computational, permit the theoretician to calculate these forces *ab initio* and then model the ensuing dynamics.

COMET XVI will highlight recent advances in the field. The conference will concentrate on modern studies of energy transfer that allow a microscopic understanding of the detailed dynamics of elastic, inelastic, and reactive events, of collision or light induced dissociation in both the gaseous and condensed phase. Some sessions will be devoted to energy transfer in highly excited molecules and in systems undergoing unimolecular or bimolecular reactions. In particular, emphasis will be given to new developments, both experimental and theoretical, in the reaction dynamics of polyatomic systems and in photodissociation processes of radicals and polyatomic molecules of interest for atmospheric-, combustion- and astro-chemistry. Studies of energy transfer in gases and liquids using time and frequency domain techniques will also be emphasized. Other sessions will examine energy transfer between chromophores in a weakly-bound complex, in hydrogen-bonded clusters, within an aggregate of helium atoms in a quantum cluster, and between solute and solvent molecules in the condensed phase. Sessions on energy transfer in reactive collisions involving ions, on atmospheric reactions of metals from meteors, on the emerging area of interest in nonadiabatic effects in chemical reactions and photodissociation are also included. An ongoing challenge for both experimentalists and theoreticians is the extension of their techniques to larger and more complex systems. A special emphasis will be devoted to the use of ultra-fast (femto-second) techniques for investigating energy transfer in gases and liquids, including complex systems as proteins.

We would like to thank the sponsors of the conference for their support. In particular we thank all the invited speakers and session chairs for agreeing to participate in the conference, and all the participants in COMET XVI, both chemists and physicists, experimentalists and theorists, coming from more than 20 foreign countries. It is a great honor to have Nobel Laureate Dudley R. Herschbach delivering the opening lecture at our meeting; to him goes our deepest gratitude.

Finally, we wish to thank all the members of the local organizing committee and in particular Nadia Balucani and Stefano Crocchianti for their dedication to the organization of the conference and related material.

Piergiorgio Casavecchia   Antonio Laganà

Conference History

Date	Conference	Site	Conference Chair(s)
1969	GRC	New Hampshire	Jeffrey Steinfeld and Charles Parmenter
1971	COMET II	Cambridge (UK)	Anthony Callear
1973	GRC	New Hampshire	C. Bradley Moore
1975	COMET IV	Loccum (Germany)	Peter Toennies
1977	GRC	New Hampshire	George Flynn
1979	COMET VI	Rodez (France)	M. Huetz-Aubert
1981	GRC	New Hampshire	Thomas George
1983	COMET VIII	Cirencester (UK)	Anthony McCaffery
1985	GRC	New Hampshire	Paul Houston and Stephen Leone
1987	COMET X	Emmetten (Switzerland)	Martin Quack
1989	GRC	New Hampshire	Eric Weitz and George Schatz
1991	COMET XII	Nijmegen (The Netherlands)	Jörg Reuss
1993	GRC	New Hampshire	David King and John Stephenson
1995	COMET XIV	Kloster Banz (Germany)	Hans-Joachim Werner and Peter Andresen
1997	GRC	Ventura, CA	Marsha Lester and Millard Alexander
1999	**COMET XVI**	**Assisi (Italy)**	**Piergiorgio Casavecchia and Antonio Laganà**
2001	GRC	USA	Hanna Reisler and Joel M. Bowman

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CONFERENCE PROGRAMME

COMET XVI

Programme

Sunday, June 20, 1999

10:00-17:00   Registration at conference desk

SESSION 1: "Dynamics of Chemical Reactions I" (Session Chair: J.J. Valentini)

17:00-17:10   Welcome, Introductory Remarks, Announcements

17:10-17:30   Overview: **J.J. Valentini** (Columbia University, New York, NY, USA)

17:30-18:10   **D.R. Herschbach** (Harvard University, Cambridge, MA, USA)
Further Adventures in Chemical Dynamics: Meditations on Fast Meteors and Slow Molecules

18:10-18:50   **D.C. Clary** (University College London, London, UK)
Quantum dynamics of polyatomic reactions

18:50-19:30   **J.P. Simons** (Oxford University, Oxford, UK)
Product State-Resolved Stereodynamics of the Endothermic Reaction $H + CO_2 \rightarrow OH + CO$

19:30-19:50   Hot topic:
P. Willis, H. Stauffer, R. Hinrichs, **H.F. Davis**
Reaction dynamics of neutral transition metal atoms with unsaturated hydrocarbons

20:15   *Dinner*

Monday, June 21, 1999

SESSION 2: "Femto-chemistry/Energy Transfer" (Session Chair: G.C. Schatz)

8:50-9:10   Overview: **G.C. Schatz** (Northwestern University, Evanston, IL, USA)

9:10-9:50   **G.R. Fleming** (University of California, Berkeley, CA, USA)
Energy Transfer in Photosynthetic Light Harvesting

9:50-10:30 **G. Scoles** (Princeton University, Princeton, NJ, USA)
Free Rotation and Rotational Relaxation of Linear Molecules in ⁴He Droplets Studied by MW, IR and MW-IR Spectroscopy

10:30-11:00 *Coffee break*

11:00-11:40 **W.H. Miller** (University of California, Berkeley, CA, USA)
Recent Developments in Semiclassical Approximations for Quantum Dynamics in Complex Molecular Systems

11:40-12:20 **T. Suzuki** (Institute for Molecular Sciences - IMS, Okazaki, Japan)
Femtosecond Time-Resolved Photoelectron Imaging

12:20-12:40 Hot topic:
L. Bussotti, **P. Foggi**, R. Righini, S. Califano
Near infrared transient absorption spectroscopy of electrons in pure water

12:40-13:00 Hot topic:
U. Manthe
Dissipative quantum dynamics in systems with strong vibronic coupling: an approach based on system-bath separation

13:15 *Lunch*

SESSION 3: "Photodissociation" (Session Chair: D. W. Chandler)

17:00-17:20 Overview: **D.W. Chandler** (Sandia National Labs, Livermore, CA, USA)

17:20-18:00 **M.N.R. Ashfold** (University of Bristol, Bristol, UK)
High Resolution Photofragment Translational Spectroscopy

18:00-18:40 **D.M. Neumark** (University of California, Berkeley, CA, USA)
Photodissociation Dynamics of I_3^- in the Time and Frequency Domain

18:40-19:20 **R.N. Zare** (Stanford University, Stanford, CA, USA)
Photofragment Polarization as a Diagnostic of Photodissociation Dynamics

19:20-19:40 Hot topic:
P.C. Samartzis, B.L.G. Bakker, D.H. Parker, **T.N. Kitsopoulos**
Photoelectron and photofragment velocity imaging following the excitation of CH_3I to the A-band using fs, ps and ns laser pulses

20:00 *Dinner*

21:15 Poster session (**MO**)

Tuesday, June 22, 1999

SESSION 4: "Energy Transfer in Clusters and van der Waals Complexes"
(Session Chair: K.J. Janda)

8:50-9:10   Overview: **K.J. Janda** (University of California, Irvine, CA, USA)

9:10-9:50   **W.C. Lineberger** (University of Colorado, Boulder, USA)
Spin-Orbit Relaxation and Recombination Dynamics in
$I_2^-(CO_2)_n$ *and* $I_2^-(OCS)_n$ *Cluster Ions: A New Type of*
Photofragment Caging Reaction

9:50-10:30   **F. Huisken** (Max-Plank-Institüt fur Strömungsforschung, Göttingen, Germany)
Vibrational Spectroscopy of Hydrogen-Bonded Complexes
in Free-Jets and Trapped in Large Helium Clusters

10:30-11:00 *Coffee break*

11:00-11:40   **M.I. Lester** (University of Pennsylvania, Philadelphia, PA, USA)
Spectroscopy and Reaction Dynamics of Hydroxyl
Radicals in Encounters with Molecular Hydrogen

11:40-12:20   **R. Naaman** (Weizmann Institute, Rehovot, Israel)
Resonance Effect in Electron Transmission through
Organized Thin Films

12:20-12:40   Hot topic:
C. Menzel, **H. Zacharias**
Internal energy of neutral ammonia clusters scattered off
LiF(100)

12:40-13:00   Hot topic:
W. Caminati, A. Dell'Erba, P.G. Favero, S. Melandri, B. Velino
Conformation, dynamics and energetics of adducts of rare gases
with fluorinated hydrocarbons

13:15   *Lunch*

SESSION 5: "Metal and Ion Reaction Dynamics" (Session Chair: D. Gerlich)

17:00-17:20   Overview: **D. Gerlich** (Technische Universität Chemnitz, Chemnitz, Germany)

17:20-18:00   **E. Murad** (Air Force Research Lab, Hanscom AFB, MA, USA)
Dynamics of Meteor Metal Reactions in the Upper
Atmosphere

18:00-18:40   **F. Vecchiocattivi** (Università di Perugia, Perugia, Italy)
Atom-Molecule Collisional Autoionization

18:40-19:20   **O. Dutuit** (Centre Universitaire d'Orsay, Orsay, France)
State-selected ion-molecule reactions with small
hydrocarbons studied with synchrotron radiation

19:20-19:40   Hot topic:
R.I. Kaiser, N. Balucani, L.C.L. Huang, O. Asvany, Y.T. Lee
*Crossed molecular beam studies on the chemical dynamics
of CN(X²Σ⁺) radical reactions with unsaturated hydrocarbons*

20:00   *Dinner*

21:15   Poster session (**TU**)

Wednesday, June 23, 1999

SESSION 6: "Dynamics of Chemical Reactions II" (Session Chair: H-J. Werner)

8:50-9:10   Overview: **H.-J. Werner** (Universität Stuttgart, Stuttgart, Germany)

9:10-9:50   **H. Reisler** (University of Southern California, Los Angeles, CA, USA)
Ion Imaging Studies of Unimolecular Decomposition

9:50-10:30   **J.M. Bowman** (Emory University, Atlanta, GA, USA)
Unimolecular reactions "under a microscope"

10:30-11:00 *Coffee break*

11:00-11:20   Hot topic:
A. Callegari, J. Rebstein, R. Jost, T.R. Rizzo
*State-to-state unimolecolar reaction dynamics of HOCl near the
dissociation threshold: the role of vibrations, rotations and IVR
probed by time- and eigenstate-resolved spectroscopy*

11:20-11:40   Hot topic:
B. Kirmse, **B. Abel**, S.Y. Grebenshchikov, R. Schinke
*Intramolecular and dissociation dynamics of NO₂: detailed
comparison between fs/ps-experiments and quantum mechanical
calculations*

11:40-12:20   **G. G. Balint-Kurti** (University of Bristol, Bristol, UK)
Wavepacket Calculations of Reactive Scattering

12:20-12:40   Hot topic:
B. Niederjohann, **E. Wrede**, K. Seekamp-Rahn, L. Schnieder,
K.H. Welge, F.J. Aoiz, L. Bañares, J.F. Castillo, B. Martinez
Haya, V.J. Herrero
*The hydrogen exchange reaction: experimental and theoretical
cross sections and the influence of the geometrical phase effect*

12:40-13:00   Hot topic:
P. Honvault, **J.-M. Launay**
*Accurate quantum dynamical calculations for the
N(²D)+H₂→NH+H reaction*

13:15   *Lunch*

Afternoon   Excursion

20:30   *Conference dinner*

Thursday, June 24, 1999

SESSION 7: "Nonadiabatic Processes" (Session chair: V. Aquilanti)	

8:50-9:10   Overview: **V. Aquilanti** (Università di Perugia, Perugia, Italy)

9:10-9:50   **D. J. Nesbitt** (University of Colorado, Boulder, USA)
                   Experimental/Theoretical Studies of State-to-state
                   Collision Phenomena: Rotational Alignment and Non-
                   Adiabatic Reaction Dynamics

9:50-10:30   **K. Liu** (Institute of Atomic and Molecular Sciences, Academia
                   Sinica, Taipei, Taiwan)
                   Crossed-Beam Studies of Elementary Chemical Reactions

10:30-11:00 *Coffee break*

11:00-11:40   **M.H. Alexander** (University of Maryland, College Park, MD,
                   USA)
                   Non-Adiabaticity in Chemical Reaction Dynamics

11:40-12:20   **G.A. Parker** (University of Oklahoma, Norman, OK, USA)
                   Quantum Reactive Scattering in Three Dimensions, Using
                   Tangent-Sphere Coordinates to Smoothly Transform from
                   the Hyperspherical to Jacobi Regions

12:20-12:40   Hot topic:
                   F.J. Aoiz, L. Bañares, J.F. Castillo
                   Spin-orbit effects in quantum mechanical rate constant
                   calculations for the $F+H_2 \rightarrow HF+H$ reaction

12:40-13:00   Hot topic:
                   Y. Teranishi, K. Nagaya, **H. Nakamura**
                   New way of controlling molecular processes by lasers

13:15   *Lunch*

SESSION 8: "Inelastic Collision Dynamics and State-selective Energy Transfer" (Session chair: A. Wodtke)	

17:00-17:20   Overview: **A. Wodtke** (University of California, Santa Barbara,
                   CA, USA)

17:20-18:00   **H.H.J. ter Meulen** (Universiteit Nijmegen, Nijmegen,
                   The Netherlands)
                   Steric Asymmetry in Inelastic Collisions of OH Radicals

18:00-18:20   Hot topic:
               P.J. Dagdigian, X. Yang
               *An experimental study of collisional rotational and
               electronic energy transfer between CN(A²Π) and Ar: Λ-doublet
               propensities and gateway effects*

18:20-19:00   **F.F. Crim** (University of Wisconsin, Madison, WI, Usa)
               ***Time and Frequency Domain Studies of Intramolecular
               Energy Transfer in Gases and Liquids***

19:00-19:40   **G.W. Flynn** (Columbia University, New York, NY, USA)
               ***Quenching Molecules with Chemically Significant Energy:
               A Quantum State Resolved Picture of the Energy Transfer
               Distribution Function***

19:40-19:55   Concluding remarks (Conference co-chairs)

20:00   *Dinner*

21:15   Poster session **(TH)**

Friday, June 25, 1999

Morning   Dispersal

LIST OF

INVITED LECTURES

AND

CONTRIBUTED PAPERS

Please note that the **Invited Lecture abstracts** are denoted by **I** and are listed following the Conference Programme sequence.

Contributed Paper abstracts (Posters and **Hot Topics)** are ordered alphabetically (first author); each abstract has a code where the number indicates the poster panel and the letters indicate the day of discussion (**MO**=Monday, **TU**=Tuesday, **TH**=Thursday); **HT** indicates Hot Topic presentation.

Consult also the author index at the end of the volume.

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ABSTRACTS OF
INVITED LECTURES
AND
CONTRIBUTED PAPERS

Further Adventures in Chemical Dynamics: Meditations on Fast Meteors and Slow Molecules

Dudley R. Herschbach

Department of Chemistry and Chemical Biology, Harvard University, Cambridge, MA 02138, U.S.A.

Scientists captivated by chemical dynamics eagerly seek out mechanistic insights, whether they lurk behind commonplace observations or require expeditions into unexplored and exotic domains. Sagas of both kinds are presented in this talk.

Everyone has seen meteors flash across the night sky, leaving a glowing trail stretching far behind. But few know that the shining trail is chiefly sodium D line emission. The venerable Chapman mechanism, proposed in 1939, postulates that Na ablated from the meteor reacts with ozone to form NaO, which then reacts with atomic oxygen to regenerate Na atoms, a large fraction of which are electronically excited. After many twists and turns, by 1986 it appeared that the Chapman proposal had been confirmed, but soon after contradictory evidence appeared. A laboratory experiment showed that in the ground electronic state NaO + O does not give an appreciable yield of excited Na. This spurred us (in collaboration with C.E. Kolb and D.R. Worsnop of Aerodyne Research) to do a beam experiment which showed that in the first Chapman step, the reaction of sodium with ozone produces, solely or almost so, a low-lying electronically excited state of NaO. Subsequently we were able to show from theory that this state could produce a large yield of excited Na atoms, and confirm that by experiment. Most recently by means of infrared diode-lasers, we found a rich spectrum of transitions from the ground to the low-lying excited NaO state. Beyond clearing up what had been a puzzle, this saga has proved rewarding because the excited NaO state at issue poses a challenge for theory, simple and striking. The molecule is quite ionic, really $Na+O^-$, so the monoxide anion has a "hole" in its valence shell. The striking fact is that in the excited state of NaO formed by the ozone reaction, this hole is aimed at the cation (i.e., the sigma orbital pointing at the cation has only one electron, the pi orbitals transverse to the internuclear axis each have two). The most plausible interpretation is that this odd result is a consequence of a stereodynamic selection rule for electron transfer from the sodium atom to an ozone orbital orthogonal to the molecular plane.

Nobody has yet seen chemical dynamics in the hyperquantum domain in which molecules acquire deBroglie wavelengths comparable to or larger than their sizes and even their distances apart. To attain that domain experimentally requires development of a source of slow molecules. That has proved feasible for atoms via laser cooling, enabling ultracold traps which have led to dramatic achievements. These include Bose-Einstein condensation and an atom laser, atom interferometry, and atom lithography, all exploiting coherent matter waves. To pursue such phenomena with molecules is an appealing prospect, since molecules offer a vast range of properties not available with atoms. In collisions involving very long deBroglie wavelengths, energy transfer processes and chemical reaction dynamics will have distinctive features, with tunneling and resonances prominent. However, for molecules it is much more difficult to reach this hyperquantum domain than for atoms. Since the forces available to trap neutral particles are weak, a key requisite is a means to lower markedly the translational kinetic energy, typically to below 1 K. For alkali atoms that is readily accomplished by repeated absorption and stimulated emission to transfer momentum in a laser-induced "optical molasses". Such a method fails for molecules because they have myriad vibrational and rotational levels, so even a dilute optical syrup is not attainable. Several means of producing molecules slow enough to trap are being pursued. Here I report progress with a dizzying but promising approach taken in our laboratory, simple in principle. It involves mounting a supersonic nozzle on a high-speed rotor, in order to cancel the flow velocity of the emerging molecules.

Quantum Dynamics of Polyatomic Reactions

David C Clary

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Recent progress in extending quantum scattering theory to chemical reactions involving more than four atoms will be described. In particular, quantum scattering calculations on the reactions of CH_4 and CH_3Cl with atoms and ions will be discussed. A particular feature will be the examination of how particular molecular vibrations, such as the CH_3 umbrella mode, influence chemical reactions. The methods are based on our rotating bond approximation (RBA) [1] which involves explicit quantum scattering treatment of bonds being broken and formed in a reaction. This method has been modified to include the umbrella vibrational modes and some rotational states [2,3].

For SN_2 reactions such as $Cl^- + CH_3Br \rightarrow CH_3Cl + Br^-$ we find the reaction is dominated by scattering resonances and the effect of the umbrella mode on the reaction is not so significant. However, for a reaction such as $O + CH_4 \rightarrow CH_3 + OH$, the effect of the umbrella vibration is dramatic. Results will also be presented on the effects of rotational states on these reactions. In addition, calculations on $Cl + CH_4 \rightarrow CH_3 + HCl$ will be reported using a new potential energy surface developed by G. Ochoa in our group.

[1] D. C. Clary, Quantum theory of chemical reaction dynamics, Science, 279, 1998,

[2] S. Schmatz and D. C. Clary, Quantum scattering on S_N2 reactions: Influence of azimuthal rotations, J Chem. Phys., 109, 1998, 8200.

[3] D. C. Clary, Quantum dynamics of the $O(^3P)+CH_4 \rightarrow CH_3+OH$ reaction, Phys. Chem. Chem Phys., 1, 1999, 1171.

Product State-Resolved Stereodynamics of the Endothermic Reaction
H + CO$_2$ → OH + CO

Mark Brouard, Dominic Hughes, Kostas Kalogerakis and John Simons

Physical and Theoretical Chemistry Laboratory, South Parks Road, Oxford OX1 3QZ, UK

The title reaction, and its exothermic reverse, has claimed more than its fair share of attention from gas kineticists, theoreticians and dynamicists over the past few decades and one could be forgiven for thinking that it might/should now be thoroughly understood. That is not so: in all respects, it is a 'complex' reaction possibly proceeding through the formation of more than one transient intermediate and involving more than one potential energy surface. The endothermic reaction has, necessarily, been studied at collision energies that lie some way above the barrier to reaction, where a very short-lived transient intermediate would be anticipated. Its rate of decay however, (following production within a van der Waals complex) into the reaction products is, apparently, reproduced by RRKM calculations. On the other hand, there is a discrepancy between the initial ultrafast kinetic measurements, which were product quantum-state resolved, and the subsequent series of measurements, which were not. Furthermore, the quantum state distributions that have been measured for the scattered products are 'colder' than those predicted by statistical theories and are sensitive to changes in the initial reagent state preparation or constraints upon their relative orientation.

In an attempt to clarify the situation, especially the possible role of reaction over excited potential energy surfaces, we have been pursuing an intensive, product state-resolved study of the stereodynamics of the endothermic reaction, using the recently established methods of polarised photon-initiation coupled with polarised, Doppler-resolved laser induced fluorescence detection. These have allowed the dynamics to be probed over a broad range of exit channel energies, extending from ca. 2700 cm^{-1} to 12000 cm^{-1} above the reaction threshold. We have discovered regular patterns in the state-resolved differential cross-sections, that establish the existence of (at least) two alternative pathways for the reaction, dependent upon the spin-orbit state of the scattered OH. This discovery has led to a re-assessment of the origin of the discrepancy between the two ultrafast studies of Wittig, and Zewail and Bernstein, which involves the possibility of scattering over an electronically excited, as well as the ground state, potential energy surface for reaction.

The OH fragments scattered into states of high rotational angular momentum, particularly the π(A") lambda-doublet component, are significantly polarised, with a propensity for 'propeller-like' motion; j$_{OH}$ tends to be aligned parallel to the scattering plane and preferentially parallel to the product velocity. This has been interpreted in terms of a simple frontier orbital model.

Comparisons will also be made with parallel studies of the iso-electronic (but exothermic) reaction
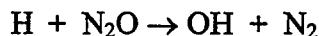
$$H + N_2O \rightarrow OH + N_2$$

Energy Transfer in Photosynthetic Light Harvesting

G. R. Fleming, B. Krueger and G. Scholes
Department of Chemistry, University of California, Berkeley
and Physical Biosciences Division
Lawrence Berkeley National Laboratory, Berkeley, California, 94720-1460, USA

Light harvesting in photosynthetic bacteria is based on a subtle interplay of electronic interactions between chromophores, coupling of the electronic transitions of these chromophores to the protein, and disorder [2]. We have investigated these systems via a combination of femtosecond nonlinear spectroscopy, electronic structure calculations and theoretical modeling. In particular we have developed the three pulse photon echo peak shift method to determine energy transfer times electron photon coupling, and the amount of disorder. We have also used femtosecond two-photon spectroscopy to probe the one-photon forbidden A_g symmetry S_1 states of photosynthetic caroteroids within the intact pigment protein complex.

From a theoretical perspective, a new method to calculate Coulombic couplings between chromopores spaced by distances smaller than their size has been introduced. The method, the transition density cube method [3] is a formally exact method of calculating Coulombic couplings and when combined with a disordered excitation model of the electronic states leads to accurate predictions of absorption and circular dichroism spectra, and of the rates and temperature dependence of energy transfer in the light harvesting 2 (LH2) complex.

We have begun to investigate plant antenna systems such as LHCII and new results on these systems will also be described briefly.

References
[1] G. R. Fleming and R. van Grondelle, Curr. Opin Struc. Biol. **7** (1997) 738-748.
[2] B. P. Krueger, G. D. Scholes, J.-Y. Yu and G. R. Fleming, Acta Physica Polonica A **95** (1999) 63-83.
[3] B. P. Krueger, G. D. Scholes, and G. R. Fleming, J. Phys. Chem. B. **102** (1998) 5376-5378.

FREE ROTATION AND ROTATIONAL RELAXATION OF LINEAR MOLECULES IN ^{4}HE DROPLETS STUDIED BY MW, IR AND MW-IR SPECTROSCOPY *.

G. Scoles

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Recent experiments on the microwave, infrared, and microwave-infrared double resonance spectroscopy of several linear molecules in superfluid ^{4}He clusters will be described. The "free" rotation of the molecules in the superfluid medium occurs with moments of inertia which are larger than when the molecule rotates in vacuum. A model based on the classical hydrodynamic motion of a rigid body in the superfluid is successful in explaining the experimental data if the variation of density of the highly quantum liquid near the guest molecule is taken into account. Furthermore, the results of all three experiments support the notion that the translational energy of the guest molecule is distributed over a set of particle-in-the-box states caused by the confinement potential of the molecule in the cluster, and indicate that relaxation over this inhomogeneous distribution greatly exceeds the rate of the rotational relaxation. The droplet size dependence of the double resonance spectra suggests a model in which rotational relaxation primarily occurs when the molecule collides with the surface of the droplet. These events appear to be in the "strong collision" regime, resulting in the molecules losing all memory of their initial rotational state when encountering the droplet boundaries.

Because the temperature of the droplets is low ($\approx$ 0.4K) and the energy exchanged in the rotationally inelastic collisions equally low, it is likely that the surface excitations of the droplet (ripplons) are involved in the relaxation. When the droplet size becomes of the order of 10^3 He atoms, the first indications appear, in the spectra, of resonances between the rotational motion of the molecules with a single excitation of the droplet.

Recent Developments in Semiclassical Approximations for Quantum Dynamics in Complex Molecular Systems

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The initial value representation (IVR) has been receiving renewed interest from several groups as a practical way of implementing the semiclassical (SC) approximation to molecular dynamics. The goal is a useful way to include quantum interference and tunneling effects into classical molecular dynamics simulations of complex processes, e.g., chemical reactions in solution, on (or in) surfaces, or in biomolecular environments. This talk reviews the SC-IVR methodology, which can also be applied to electronically non-adiabatic processes, and describes its recent applications and prognosis.

Femtosecond Time-Resolved Photoelectron Imaging

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Abstract

Femtosecond time-resolved photoelectron imaging (FS-PEI) is presented for the first time. This novel method allows routine measurement of the speed and angular distribution of photoelectrons with unit collection efficiency and ultrafast time-clocking.

The $S_1(^1B_{3u})$ state of pyrazine is a well-known example of an intermediate case in radiationless transition. It is predicted that broad-band coherent excitation of an intermediate case molecule provides biexponential fluorescence decay where the first component is the dephasing of an optically-prepared singlet state into the mixed singlet-triplet character and the second component is the population decay of this mixed state. In the 1980's, biexponential fluorescence decay of S_1 pyrazine was extensively studied, and lengthy debate ensured as to whether the fast decay was due to dephasing or Rayleigh-Raman scattering. We employed [1+2'] FS-PEI and observed the phototelectron scattering distribution for a number of pump-probe time delay. As shown below, photoelectron scattering distributions were bimodal, in which the high and low-speed components were assigned to the ionization from the singlet and triplet characters, respectively. The singlet character decayed in 100 ps, while triplet character showed corresponding growth, providing direct evidence for dephasing.
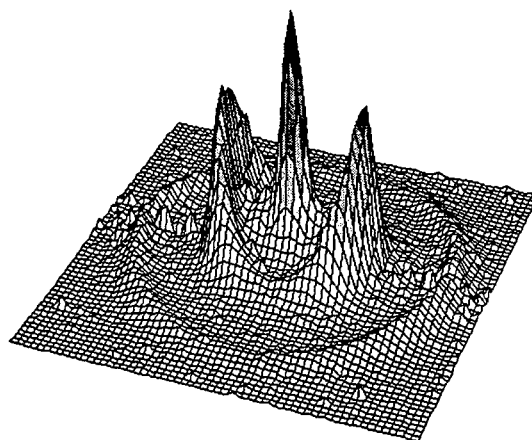
Photoelectron scattering distribution (Abel-transform of the image; at t=2ps).

High Resolution Photofragment Translational Spectroscopy

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The technique of H (Rydberg) atom photofragment translational spectroscopy (HRPTS) is providing ever more detailed insights into the primary photochemistry of molecular hydrides.[1,2] This presentation will highlight some of the capabilities of the technique, then concentrate on a number of recent studies that have been made possible by improvements in our Lyman-α generation efficiency (through the use of phase matched frequency tripling methods). This has allowed new investigations of the *angular dependence* of recoiling H atoms resulting from at 121.6 nm photolysis of a several prototypical hydrides, including HCN, H_2S, CH_4, C_2H_6, and various of their deuterated analogues. Such measurements, particularly if allied with *ab initio* data for the relevant excited state potential energy surfaces, afford some of the most detailed insights yet available into the factors controlling these fragmentation processes.

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Photodissociation dynamics of I_3^- in the time and frequency domain

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The photodissociation dynamics of I_3^- were investigated using two complementary techniques, femtosecond photoelectron spectroscopy (FPES) and fast ion beam photofragment translational spectroscopy (FIBPTS). In the FPES experiment, I_3^- is excited by a femtosecond pump pulse at 390 nm and the resulting dynamics are followed by time-resolved photoelectron spectroscopy. FIBPTS is a frequency domain experiment in which the I_3^- is dissociated at several wavelengths and the product velocity distribution is determined using a coincidence detection scheme. The two experiments yield the time scale of formation for the I_2^- and I^- products as well as the vibrational distribution of the I_2^-. In addition, they show that I^- is produced by a concerted three-body dissociation mechanism. The I_2^- vibrational distribution and the I_2^-/I^- branching are very different from previous liquid phase results on I_3^- photodissociation in ethanol.

Photofragment Polarization as a Diagnostic of Photodissociation Dynamics

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Interference patterns resulting from diffraction experiments permit the structure of an object to be deduced. For example, the fringe pattern from the celebrated Young's double-slit experiment can be used to determine the size and separation of the slits, and the X-ray or electron diffraction pattern from crystals are used to infer molecular structure. These diffraction patterns are caused by the constructive and destructive interference of waves from multiple pathways. Chemical processes, such as energy transfer, reactive scattering, and photodissociation, can also take place through multiple pathways and can thus display interference phenomena. One of the manifestations of the matter-wave interference of these pathways is that the angular momentum of each photofragment can possess handedness (helicity) so that the photofragments possess topspin or backspin. As such, the measurement of handedness in the angular momentum of photofragments directly measures the interference between dissociating pathways. An illustration of this general phenomena is the photodissociation of iodine monochloride in which the $Cl(^2P_{3/2})$ photofragments possess orientation that oscillates as a function of the photolysis wavelength. The behavior is general and can become a new type of spectroscopy for unbound states.

Spin-orbit relaxation and recombination dynamics in $I_2^-(CO_2)_n$ and $I_2^-(OCS)_n$ cluster ions: A new type of photofragment caging reaction

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Abstract

We report a new type of photofragment caging reaction that is only possible because of the strong solvent-induced perturbation of the inherent electronic structure of the chromophore. The photoexcitation of I_2^- at 395 nm promotes it to a dissociative state correlating with $I^- + I^*(^2P_{1/2})$, the only near-UV dissociation channel for unsolvated I_2^-. In $I_2^-(CO_2)_n$ and $I_2^-(OCS)_n$ clusters, interaction with the solvent is observed to result in extremely fast spin-orbit relaxation. In general, we detect three reaction pathways: (1) direct dissociation of the chromophore to $I^- + I^*(^2P_{1/2})$; (2) the $I_2^- \rightarrow I^- + I^*$ dissociation, followed by spin-orbit quenching leading to $I^- + I(^2P_{3/2})$ products; and (3) the $I_2^- \rightarrow I^- + I^*$ dissociation, followed by spin-orbit quenching and $I^- + I(^2P_{3/2}) \rightarrow I_2^-$ recombination and vibrational relaxation. We present experimental evidence of the spin-orbit relaxation and caging and discuss possible mechanisms. The results include: the measured translational energy release in 395 nm photodissociation of unsolvated I_2^- indicating that solvation-free dissociation proceeds exclusively via the $I^- + I^*$ channel; ionic product distributions in the photodissociation of size-selected $I_2^-(CO_2)_n$ and $I_2^-(OCS)_n$ clusters at the same wavelength, indicating the above three reaction channels; and ultrafast pump-probe measurements of absorption recovery, indicating picosecond time-scales of the caging reaction. We rule out the mechanisms of spin-orbit quenching relying on I^*-solvent interactions without explicitly considering the perturbed electronic structure of I_2^-. Instead, the spin-orbit relaxation occurs by electron transfer from I^- to $I^*(^2P_{1/2})$, giving $I(^2P_{3/2}) + I^-$. The 0.93 eV gap between the initial and final states in this transition is bridged by differential solvation due to solvent asymmetry.
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VIBRATIONAL SPECTROSCOPY OF HYDROGEN-BONDED COMPLEXES IN FREE JETS AND TRAPPED IN LARGE HELIUM CLUSTERS

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The vibrational spectroscopy of small hydrogen-bonded clusters has been studied in molecular beams employing the molecular beam depletion (MBDS) technique which is based on the vibrational predissociation of weakly bound complexes after infrared laser excitation [1]. A unique feature of the experimental setup is the possibility to select the clusters according to their size, by dispersing the primary cluster beam with a secondary rare gas beam and measuring the laser-induced depletion as a function of the scattering angle. The spectral region around 3 μm (2800 - 3800 cm^{-1}) is accessed with a Nd:YAG-laser-pumped optical parametric oscillator (OPO), enabling us to excite various C-H, O-H, N-H, and H-F stretching vibrations. The lecture will focus on the pecularities of the molecular depletion technique and emphasize the importance of size selection. From the many systems, particularly interesting examples, $(H_2O)_n$ [2] and water clusters doped with methanol [3], will be chosen to demonstrate the power of the technique and to present most recent results.

In a new series of experiments, the same complexes, that have been studied before as size-selected isolated gas phase species, were trapped in large liquid helium clusters (He_N). These nano-sized systems were prepared under molecular beam conditions, by employing the pickup technique and doping the He_N host clusters with the molecules of interest. If two or more molecules are captured by the host cluster they interact through their permanent dipole moment and form the desired complexes. With this technique, which may be termed *nano-matrix spectroscopy*, it is possible to produce binary and even larger complexes (embedded in the helium cluster) at extremely low vapor pressure of the chromophore molecule (10^{-6} - 10^{-5} mbar). While the first experiments along this line were conducted for $(H_2O)_n$ trapped in He_N [4], the most recent studies were devoted to molecules and complexes which play an important role as prototypes of larger biological systems. New experimental results obtained for formic acid (FA) and glycine (Gly) as well as their dimers and their complexes with water will be presented and compared with theoretical predictions.

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Spectroscopy and Reaction Dynamics of Hydroxyl Radicals in Encounters with Molecular Hydrogen

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The OH + H_2 → H_2O + H reaction is a prototypical example of reactions in which hydroxyl radicals abstract hydrogen atoms from hydrocarbons to form H_2O in atmospheric and combustion environments. This laboratory is examining this fundamental reaction from a new perspective by initiating the inelastic or reactive scattering event from a restricted range of orientations between the OH and H_2 partners. This is accomplished by trapping the reactants in a shallow intermolecular well located in the entrance channel and promoting the scattering dynamics through electronic or vibrational activation of the OH or H_2 partner.

Electronic excitation of OH in the presence of H_2 facilitates a nonradiative decay process that rapidly removes OH from its excited $A\ ^2\Sigma^+$ electronic state. Quenching may proceed by a non-reactive pathway that generates ground state OH $X\ ^2\Pi$ + H_2 or by a reactive pathway that produces H + H_2O. Doppler spectroscopy of the H-atom products demonstrates that reactive quenching is a significant decay channel. A bimodal translational energy distribution is observed, which is attributed to two different dynamical pathways through the conical intersection that funnels OH $A\ ^2\Sigma^+$ + H_2 into H + H_2O.

Infrared or stimulated Raman excitation of the OH or H_2 partners within OH-H_2 reactant complexes in their ground electronic state supplies sufficient energy to surmount the activation barrier and thereby may induce chemical reaction. Alternatively, vibrational excitation may cause the weak intermolecular bond to break, initiating an inelastic scattering event. Direct time-domain measurements show how long the initial excitation stays localized in the OH or H_2 oscillator prior to inelastic scattering or chemical reaction, while OH (v=1) product rotational distributions reveal the inelastic scattering dynamics. Analogous studies are underway for the OH + CH_4 system.

Resonance Effect in Electron Transmission through
Organized Thin Films.

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Experiments will be described in which photoelectrons are transmitted through organized organic films and the energy of the transmitted electrons is analyzed. Variations in the transmission probability as a function of energy may be caused by several phenomena. In general, the transmission is governed by the band structure. The bands are formed by anion states (the neutral film and the extra photoelectron) that interact strongly due to the large radii of the orbitals associated with these quasibound states.

In addition to the band structure, variations in the transmission probability may be caused either by localized or non-localized states. Among the localized states that affect the transmission are long lived resonance states on the molecules and imperfections in the monolayer that forms traps. The variations can be caused also by simple quantum mechanical interferences that are produced due to the periodicity in the structure of the film. This last effect is produced by the non-localized nature of the electron. The relation between the experimental observations and the structural parameters that produce it will be discussed.

Dynamics of Meteor Metal Reactions in the Upper Atmosphere

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ABSTRACT

The objective of this review is to provide a summary of the chemical reactions that occur when metal atoms are released in the upper atmosphere when meteoroids enter the Earth's atmosphere. The most studied of these metal atom reactions are those connected with sodium - this largely arises because of the extensive database of sodium airglow (both nightglow and dayglow) observations. In the nightglow a faint emissions due to NaD line is observed at night:

$$Na\ (^2P_{1/2,\,3/2}) \rightarrow Na\ (^2S_{1/2}) + h\nu \quad (1)$$
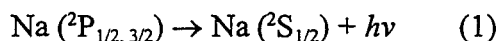
The origin of the Na $(^2P_{1/2,\,3/2})$ is now understood to be due to the sequence of reactions first proposed by Chapman[1]:

$$Na + O_3 \rightarrow NaO + O_2 \quad (2)$$
$$NaO + O \rightarrow Na\ (^2P_{1/2,\,3/2}) + O_2 \quad (3)$$
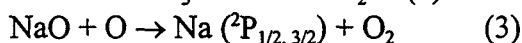
followed by reaction (1) above. Thermochemical measurements of the dissociation energy of NaO indicated that the sequence of reactions (1) and (2) is exothermic enough to explain the observed nightglow emission.[2] The rate constant for reactions (2) and (3) were calculated by Kolb and Elgin to be 3.4×10^{-10} and 1×10^{-10} cm^{-3} s^{-1}, respectively.[3] Later analysis by Bates and Ohja[4] raised questions about reaction (3) based on symmetry arguments. Specifically, they pointed out that reaction (3) can give rise to both Na $(^2P_{1/2,\,3/2})$ and Na $(^2S_{1/2})$ in a ratio of 1-to-3; this ratio, f, is then sufficient to provide agreement between the observed and calculated airglow intensities based on the Chapman mechanism. However, experimental measurements in a flow tube apparatus of this ratio assuming that both NaO and O are in their ground states ($^2\Pi$ and ^3P) indicated f to be ~ 0.01,[5] raising questions about the validity of the Chapman mechanism. The conundrum was resolved by Herschbach et al. and Shi et al. who found that in a beam experiment NaO is formed preferentially in the A $^2\Sigma^+$ state, which correlates with Na $(^2P_{1/2,\,3/2})$.[6-8] Other metals, such as Mg and Fe, are more important in meteor composition than Na, and much work has been done on the kinetics of their reactions. However, the detail with which these metals have been studied much less than that of Na for several reasons: the airglow data are not as extensive, the molecular states are much more complex, and the application of thermochemical modeling to the meteors is complicated by the higher boiling points of the oxides of Mg and Fe. These issues will be discussed as time permits.

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ATOM-MOLECULE COLLISIONAL AUTOIONIZATION

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Thermal energy collisions of metastable rare gas atoms with atomic or molecular targets can lead to a spontaneous electron ejection. The basic requirement is that the two partners should have enough internal energy to produce an autoionizing collision complex. This collisional autoionization is often called Penning ionization or chemiionization and has long attracted the attention of the scientific community, and two recent review articles have summarized the most important conclusions which have been drawn [1,2].

Several experimental techniques are used to study the microscopic dynamics of these processes: elastic scattering can provide information on the collision dynamics up to the electron emission, Penning ionization electron spectroscopy can lead to an excellent insight on the internal state distribution in the ionic collision complex, and Penning ionization optical spectroscopy allows the characterization of the vibronic states of the excited species when formed. However mass spectrometric studies are necessary, through the identification of the nature of the final ions produced in the collision, to verify the occurrence of dissociations or associations or even chemical reactions between the collision partners before or after the ionization event. Moreover the measurement of the energy dependence of the partial cross sections for the possible ionization channels can provide information for the description of the collision dynamics after the ionization is occurred.

In our laboratory these cross sections are measured in a crossed beam apparatus which schematically consists of a vacuum chamber system where two beams, one of velocity selected metastable rare gas atoms and the other of target molecules, cross each other in a well defined collision volume. The product ions are then mass analyzed and detected. Very recently an electron energy analyzer which allow to measure electron energy spectra has been also added.

The experimental results so obtained allow us to obtain very detailed results about the dynamics of these processes. Some recent results will be presented at the meeting, with also some very recent succesful attempts of measuring the angle and energy distributions of product ions by velocity-ion-imaging technique, performed in the laboratory of D.H. Parker in Nijmegen [3], in collaboration with our laboratory in Perugia.

The results show that very often the dynamics is strongly affected by the anisotropy of interaction [4]. This has been directly confirmed in a recent experiment performed in Osaka, in the laboratory of T. Kasai, in collaboration with our group, where the ionization of methyl chloride molecules by metastable argon atoms has been studied orienting the molecules during the collision at thermal energy.

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State-selected ion-molecule reactions with small hydrocarbons studied with synchrotron radiation

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The study of reaction cross sections as a function of both internal and collision energy is essential to understand their mechanisms. Our experimental set-up allows both approaches by combining two techniques. Reactant ions are formed by photoionisation with synchrotron radiation in the vacuum ultraviolet range and selected in continuously variable internal energy with a coincidence technique. The collision energy can be varied from nearly thermal energy to 20 eV in the laboratory frame by a radiofrequency octopole ion guide technique. More detailed information about reaction mechanisms is obtained from isotope effects with partially deuterated reactants and from product time-of flight spectra.

Another PEPICO experimental set-up equipped with a supersonic molecular beam crossing the monochomatized synchrotron VUV radiation allows us to study unimolecular reactions. It is another way of probing the reacting potential energy hypersurface by photoionizing Van der Waals molecules formed with the two neutral reactants and comparing fragmentation patterns with the bimolecular reaction products.

The example of the reaction between acetylene ions and ethane will be presented, in particular the H and H$^-$ transfer channels. Our results show that these two reaction channels involve a rather short-lived $C_4H_8^+$ intermediate complex. This complex has a lifetime which is not long enough to allow isotopic scrambling of the hydrogen atoms. In contrary the other reaction channels have been reported to involve a long-lived intermediate complex, which is the butene ion. We have also looked for possible H$^-$ transfer inside mixed acetylene-ethane clusters, but only the reaction products resulting from the long-lived complex dissociation were observed.

ION IMAGING STUDIES OF UNIMOLECULAR DECOMPOSITION

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Selected aspects of the photoinitiated unimolecular decomposition of jet-cooled molecules will be discussed, emphasizing both scalar and vector properties. Results from several complementary experiments will be presented: radiationless decay of the initially excited electronic state, photofragment yield spectroscopy, branching ratios, and correlated and angular distributions obtained via photofragment ion imaging. The results will be discussed in terms of vibronic levels of mixed electronic character coupled directly or via radiationless decay to the various continua and exhibiting several distinct time scales. Specifically the dissociation of NO_2 and HNCO will be described, with emphasis on processes that occur at long range. In the former case, the correlation of fragments spatial distributions with their internal and translational states will be treated in terms of a simple classical model based on angular momentum conservation. In the case of HNCO, emphasis will be placed on the threshold region of the H + NCO channel, where both large centrifugal barriers and competition with the triplet channel (^{3}NH + CO) are manifest.

Unimolecular reactions "under a microscope"

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I will describe recent, multi-group* calculations and experiments on the rotational dependence of the resonance energy and width of $HOCl(6nOH, J, K) \rightarrow Cl+OH$. The calculations use a recently developed, very accurate ab initio potential energy surface [S. Skokov, J. M. Bowman, and K. A. Peterson, J. Chem. Phys. 109, 2662, (1998)] and a variety of calculational methods. Calculations for non-zero total angular momentum are done using the adiabatic rotation approximation, which will be shown to be highly accurate for HOCl. The variation of the resonance width with J and K will be shown to be due to rotation-induced coupling of the 6nOH state to a dense set of OCl excited states. A simple model describing the coupling of the 6nOH state with backround states, using a coupling constant on the order of 0.05 cm-1 will be given and shown to give a qualitatively correct picture of the fluctuation of the resonance width with J. Finally, the energies of many non-overlapping resonances, some of which are assigned, for J=18 and K=0 will be presented and compared to RRKM theory, which overestimates the average dissociation rate by an order of magnitude

* Sergei Skokov (Emory), Kirk Peterson (Washington and PNNL), C.-Y. Yang and Stephen Gray (ANL), Vladimir Mandelshtam (UCI), Remy Jost (Grenoble), Marc Joyeux (Grenoble)

Wavepacket Calculations of Reactive Scattering

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and

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The calculation of reactive scattering cross sections using wavepackets will be outlined. The nature of wavepackets will be discussed and it will be shown how cross sections over a large energy range may be obtained from a single calculation. Techniques for analysing the wavepacket dynamics to extract the reactive scattering cross sections will be described. The use of finite grids to describe the wavepacket motion and several methods designed to overcome the limitations associated with the use of such grids will be described.

A new highly efficient and technically simple method of quantum wavepacket dynamics will be presented. The advantage of the method is that it requires only the real part of the wavepacket and that the propagation of the wavepacket is computationally more efficient.

Results will be presented for the reactions
1) $O+H_2 \rightarrow OH + H$ and its isotopic variants.
2) $O + HCl \rightarrow OH + Cl$
3) $Li + HF \rightarrow LiF + H$.

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Experimental/Theoretical Studies of State-to-state Collision Phenomena: Rotational Alignment and Non-Adiabatic Reaction Dynamics

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This talk will present results from recent work in the following two areas of i) collisional alignment of rotational states and ii) nascent state distributions and non-adiabatic reactive scattering dynamics in prototypic H atom abstraction reactions.

First of all, classical trajectory calculations have been performed on experimentally determined intermolecular potentials for $He-O_2$, $He-CO$, and $He-CO_2$, in order to simulate the collisional formation of rotationally aligned molecular distributions in a supersonic expansion. These calculations verify that multiple collisions between the light "diluent" gas and heavier "seed" rotor molecules result in a distribution of rotor molecules with negative alignment ($a_2 < 0$), i.e., a preference for $\mathbf{j}$ perpendicular to the expansion axis. The asymptotic alignment is observed to depend strongly on the angular momentum, increasing monotonically with j. In addition, collisional formation of the alignment is found to reflect comparable contributions from both elastic (m_j-changing) and inelastic (j-changing) collisions. Finally, the dependence of rotational alignment on final speed distributions in the jet will be discussed.

Secondly, the reaction of $F + n-H_2$ to form $HF(v,J) + H$ has been studied in a crossed jet apparatus under single collision conditions, with high-resolution direct absorption spectroscopy used to probe the nascent rovibrational HF distributions. Furthermore, the J-dependent reactive cross sections into $HF(v=3,J)$ are investigated over a range of center-of-mass collision energies well *below* the 1.9 kcal/mole barrier for *adiabatic* chemical reactions with *ground state* $F(^2P_{3/2})$ atoms, and therefore isolating the *non-adiabatic* contributions from *spin orbit excited* $F^*(^2P_{1/2})$. Wherever possible, the results of these collision energy and quantum state resolved studies will be directly compared with numerically exact quantum scattering calculations on state-of-the-art potential surfaces.

Crossed-Beam Studies of Elementary Chemical Reactions

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The recent crossed-beam investigations of two prototypical reactions in our laboratory will be presented in this talk. The first reaction $S(^1D) + H_2 \rightarrow SH + H$ is believed to proceed solely through an insertion mechanism, involving an intermediate H_2S complex. Despite the deep well (~90 kcal/mol with respective to the SH + H product channel), the rotational distribution of the SH product was found to be bimodal, indicative of a nonstatistical behavior. More intriguingly, this bimodality exhibits a strong dependence on product scattering angles. Possible implications about the dynamics of complex-forming reactions will be discussed. The second reaction $Cl(^2P) + H_2 \rightarrow HCl + H$ is a direct abstraction reaction with a collinear barrier. The effects of the reagent rotation (H_2, j = 0 and 1) and the spin-orbit state (Cl, $^2P_{3/2}$ and $^2P_{1/2}$) on its reactivity will be highlighted. It was found that the rotation of H_2 has positive impact in promoting the reaction, and that the spin orbit excited $Cl^*(^2P_{1/2})$ atom is more reactive than the ground state $Cl(^2P_{3/2})$. The detailed dynamical attributes (state and angular distributions) for both spin-orbit states are also elucidated and contrasted.

Non-Adiabaticity in chemical reaction dynamics

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We will describe fully-quantum scattering studies of nonadiabaticity in the F + H_2 reaction. Because of its experimental accessibility this is the paradigm for exothermic triatomic reactions. The two important questions we wish to address are: (1) what is the reactivity of the excited ($^2P_{1/2}$) spin-orbit state and (2) how well is the dynamics of the reaction described by calculations on a single, electronically adiabatic potential energy surface. (The barrier on the most-recent *ab initio* PES including the spin-orbit Hamiltonian is ≈ 1.9 kcal/mol while the spin-orbit splitting in the F atom is 1.15 kcal/mol).

Crossed beam studies indicate that the reactivity of the excited spin-orbit state is negligible at collision energies below ≈ 2 kcal/mol. Nothwithstanding, recent IR absorption experiments offer a new means to explore the reactivity of the spin-orbit excited F atoms.

There have been a number of theoretical investigations of the role of the excited electronic PES's in the F+ H_2 reaction. The lowest electronic state [$1^2A'$ ($^2\Sigma^+$ in linear geometry) correlates with the product electronic ground state, while the two other electronic states ($2^2A'$ and $1^2A''$ ($^2\Pi$ in linear geometry)] correlate with excited electronic states of the products and are energetically inaccessible in the product arrangement channels.

Although quantum scattering studies have been reported by several groups, these calculations have been subject to various approximations, both in the treatment of the dynamics as well as PES's and couplings (non-adiabatic, coriolis, spin-orbit).

We have extended earlier investigations making use of sophisticated MRCI PES's. As compared to the simpler, single PES calculations which neglect the open-shell character of the reaction, it is necessary to include six electronic states in the reactant arrangement and two in the product arrangements. Spin-orbit and coriolis coupling were treated exactly.

Scattering calculations were carried out at a large number of energies. The latest results will be presented and discussed at the meeting.

Quantum Reactive Scattering in Three Dimensions, Using Tangent-Sphere Coordinates to Smoothly Transform from the Hyperspherical to Jacobi Regions

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Hyperspherical coordinates are well suited for treating rearrangement processes in the strong interaction region and several different hyperspherical coordinates have been successfully used for quantum reactive scattering by various research groups. However, it is well known that asymptotically the appropriate set of coordinates are the three (for a three particle system) set of Jacobi coordinates. We will show how one can smoothly connect the hyperspherical coordinates in the exchange region to Jacobi coordinates in the non-exchange region using tangent-sphere coordinates. This reduces the computational time to solve the quantum Schrodinger equation, eliminates the matching region, and also allows one to use variational techniques such as the Kohn-variational method.

Steric Asymmetry in Inelastic Collisions of OH Radicals

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Measurement of the steric asymmetry in inelastic and reactive scattering provides detailed information about the interaction potential. In addition to the velocity and the initial internal energy states of the collision partners the relative molecular orientation is a most determining factor for the outcome of the scattering process. However, whereas for many molecules the velocity and the initial energy state are precisely controllable by molecular beam and laser techniques, this is somewhat more problematic for the molecular orientation. In case of a permanent electric dipole moment molecules can be oriented in an electric field, but usually the achievable orientation is limited due to the occupation of different M_J substates. Moreover a strong Stark effect is a prerequisite in order to obtain a sizeable orientation.

The open shell molecule OH is an extremely relevant candidate for the study of steric asymmetries in inelastic and reactive scattering processes. This free radical plays an important role as a short lived intermediate species in reactive processes, such as in the Earth's atmosphere, in plasmas and in combustion processes. At present various reactions involving OH form the subject of extensive theoretical research based on *ab-initio* potentials. A comparison of theoretical cross sections for scattering of oriented OH with experimental data gives direct information about the reliability of the used interaction potential. Moreover. the OH radical has a relatively large electric dipole moment and a strong Stark effect, particularly for the lowest Λ-doublet states, which makes it suitable for orientation experiments.

The present work reports on the state preparation and orientation of OH radicals. and their application for the measurement of steric effects in inelastic collisions with a variety of atoms and molecules. Subsequent to the production and state preparation in a pulsed supersonic expansion followed by electrostatic state selection, as described in detail before, the OH molecules are oriented in a homogeneous electric field. Mainly the $J = M_J = 3/2$, upper Λ-doublet state is populated, for which an optimal orientation could be obtained. Scattering of the oriented molecules was studied in single collisions with Ar, He, H_2, CO, and N_2 in a pulsed secondary beam. By orienting either the O side or the H side towards the collision partner steric effects could be studied for collision induced transitions from the rotational ground state to excited rotational states in both the F_1 and F_2 ladder.

Large steric effects were observed for transitions to high rotational states in the F_1 ladder, especially for the heavier collision partners. The transition probability is larger for collisions at the H side compared to O side collisions, which can be expected from a classical point of view. Differences up to a factor 5 were measured. For transitions to the F_2 ladder, however, no general behavior is observed; the steric effects are different for each collision partner and also the O side is prefered in some transitions. Possibly quantum interference effects due to the difference between the two potential surfaces $V_{A'}$ and $V_{A''}$ governing the collision process play an important role, as is the case in collisions of randomly oriented OH molecules.

Time and Frequency Domain Studies of Intramolecular Energy Transfer
in
Gases and Liquids

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Vibrational overtone excitation produces molecules with enough energy to overcome typical barriers in chemical reactions. Frequency-resolved measurements, which give the vibrational overtone excitation spectrum, reveal the couplings within a molecule and, hence, the flow of energy out of a zero-order state *if it were to be excited*. Time-resolved measurements, in which a short laser pulse actually prepares the zero-order state, provide similar information in the time domain by following the flow of energy out of an initially excited high frequency vibration.

The *frequency domain* experiments obtain the vibrational overtone excitation spectrum of isocyanic acid (HNCO) molecules cooled in a supersonic expansion by monitoring one of the products of their photodissociation. The well-resolved spectrum reveals systematic patterns of interactions in the molecule and allows the identification of the interacting states and the strengths of their couplings in the region of three, four, and five quanta of N-H stretching vibration. Matrix elements of 10 cm^{-1} to 20 cm^{-1} couple the N-H stretching zero-order state to other states having one quantum of N-H stretching excitation replaced by multiple quanta of lower frequency vibrations.

The *time domain* measurements use short laser pulses to prepare and observe the evolution of a non-stationary state of a molecule in either a gas or a solution. The *gas phase* measurement uses one pulse to excite the first overtone of the O-H stretching vibration in nitric acid (HONO$_2$) and a second pulse to dissociate molecules in which energy has flowed out of the O-H stretch. Observation of fluorescence from the NO$_2$ dissociation product at different intervals between the vibrational overtone excitation and the dissociation pulses shows that energy flows out of the initially excited O-H stretching state in about 12 ps, a result that is consistent with a simple Golden Rule calculation. In the *solution* measurement, one pulse excites the first overtone of the C-H stretch of methylene iodide (CH$_2$I$_2$) in CCl$_4$ and another probes the vibrationally excited molecule by electronic absorption. Because absorption of the second photon requires energy to have left the initially excited C-H stretch, the time evolution of the absorption reflects the flow of energy into other parts of the molecule and, eventually, into the solvent. The time evolution depends on the probe wavelength, with a typical growth of about 10 ps and a decay ranging from 30 to 70 ps as the probe energy changes by 1600 cm^{-1}.

Quenching Molecules with Chemically Significant Energy: A Quantum State Resolved Picture of the Energy Transfer Distribution Function

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Our work over the past few years has focused on efforts to understand, at the quantum state resolved level, the quenching of unimolecular reactions. The study of this problem is one aspect of the more general field of vibrational energy transfer, the process by which molecules transfer their internal vibrational energy during collisions. Because unimolecular reactions involve the breakup of molecules with sufficient vibrational energy to undergo bond rupture, the energy transfer processes involved are often referred to as taking place at "chemically significant" energies. The infrared diode laser probe method, which we have developed for monitoring these high-energy collision events, is an exceedingly powerful technique that provides a wealth of interesting dynamical information.

Our main research effort is aimed at developing an understanding of the quantum state resolved picture of the quenching process. In addition to obtaining information about this quenching mechanism, we have recently developed *a direct inversion procedure* that allows us to convert our quantum state and velocity resolved scattering data into a P(E,E') energy transfer probability distribution. P(E,E') is simply the distribution function that gives the probability for relaxing a highly excited molecule of initial energy E to a final energy E' in the collisional quenching process. The importance of this distribution function and methods to obtain it directly from experimental data are difficult to exaggerate. Our method for obtaining P(E,E') employs a direct inversion of experimental data that can in turn be compared to any theoretical model.

In the experimental approach that we are using to study these energy transfer processes, substrates (S) of essentially arbitrary complexity are produced with high energy by laser pumping methods. The collision processes that relax these highly excited S* molecules are investigated by probing the quantum states of a bath molecules B produced by the collision between S* and B. By using relatively simple bath molecules and sophisticated laser probe methods to follow the quantum states of B, the nature of the mechanism for energy loss by S* can be "seen" through the behavior of the (small) energy acceptor molecule, B.

Soft Collisions and Impulsive Collisions

Collisions that produce vibrationally excited states of the bath acceptor have been shown to occur at relatively long range as they are accompanied by very little rotational excitation or translational energy recoil. This observation suggests that long range forces such as dipole-dipole interactions are dominating the excitation of the vibrational modes of the bath, quite a surprising and unexpected result. On the other hand, collisions that leave the recoiling bath molecule in the ground vibrational state but with considerable rotational excitation are observed to occur with large translational recoil. These impulsive collisions clearly dominate the energy loss mechanism.

The P(E,E') Energy Transfer Distribution Function

Of particular interest is a comparison of P(E,E') distributions for the molecules pyrazine, 2-methylpyrazine, and hexafluorobenzene having 5 eV of internal energy, relaxed by carbon dioxide. In all three donor molecules single collisions with $\Delta E \geq 5,000$ cm^{-1} are clearly evident. At $\Delta E = 5,000$ cm^{-1} P(E,E') decreases noticeably going from pyrazine to hexafluorobenzene to methylpyrazine. On the other hand, at $\Delta E = 2,500$ cm^{-1} the exact opposite trend is observed. Since P(E,E') is a normalized distribution, these shifts in amplitude versus ΔE show that the probability distribution changes from molecule to molecule. So far the shifts seem to be correlated with the density of vibrational states in the donor molecule. With an increase in low frequency modes going from pyrazine to hexafluorobenzene to methylpyrazine, the probability distribution shifts its amplitude to favor smaller ΔE values. This suggests that the high energy "super collision" tail of P(E,E') is maximized for stiff molecules with mostly high frequency vibrations.

The reaction Cl + H$_2$: A crossed molecular beam, quasiclassical trajectory and quantum mechanical scattering study

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The reaction
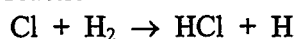
$$Cl + H_2 \rightarrow HCl + H \qquad\qquad \Delta H^\circ_0 = 1.03 \text{ kcal/mol}$$

besides its fundamental interest, is a prototype for a host of Cl reactions that are important in atmospheric chemistry. Experimental work on the rate constants is very extensive. Instead, cross sections were unavailable until lately.[1] Converged quantum mechanical (QM) scattering calculations were reported for the first time in 1991.[2]

We report differential cross sections (DCS) at collision energies E_c=5.85 kcal/mol and E_c=4.25 kcal/mol for

$$Cl(^2P_{3/2,1/2}) + n\text{-}H_2(v=0, j=0,1,2,3) \rightarrow HCl(v'=0, \text{all } j') + H$$
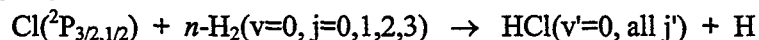
and at E_c=6.3 kcal/mol for

$$Cl(^2P_{3/2,1/2}) + n\text{-}D_2(v=0, j=0,1,2,3) \rightarrow DCl(v'=0, \text{all } j') + H$$
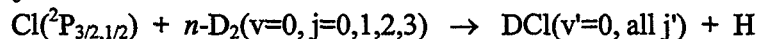
$Cl(^2P_{3/2,1/2})$ beams are generated by a radio-frequency discharge source starting from dilute mixture of Cl_2 in He or Ne. The spin-orbit state distribution is characterized by Stern-Gerlach magnetic analysis: the beam contains ~20% of excited $Cl(^2P_{1/2})$, which is located 2.5 kcal/mol above the ground state.[3] The experimental results are compared with those of scattering calculations of state-to-state $(v,j \rightarrow v',j')$ DCS based on accurate QM methods as well as the quasiclassical trajectory (QCT) method, in both cases using the G3 potential energy surface (PES).[4]

The agreement between experiment and theory for Cl+H$_2$ at E_c=5.85 kcal/mol is rather good, although not perfect: using the theoretically predicted fraction of energy in translation (about 80%), the wings of the experimental angular distribution are somewhat underestimated.[1] Interestingly, a reactivity of the excited rotational levels of H$_2$ (present in our beam) higher than predicted by the G3 PES with respect to j=0, as shown by very recent studies of the reaction excitation function by Liu and coworkers,[5] could account for the small difference between experiment and theory.

Considerable disagreement between experiment and theory is noted for Cl+D$_2$ at E_c=6.3 kcal/mol, where experiments show more sideways scattering than predicted by QM calculations, suggesting that the bending potential of the G3 PES is perhaps too repulsive.

Finally, a large disagreement between experiment and theory is noted for Cl+H$_2$ at E_c=4.25 kcal/mol: here, the lab angular distribution is much more backward scattered (with respect to the Cl direction) than predicted by QM calculations. Even assuming a reactivity of H$_2$(j=1) comparable or larger than that of H$_2$(j=0) cannot account, on energetic grounds, for the discrepancy. Interestingly, assuming some reactivity of the spin-orbit excited $Cl(^2P_{1/2})$ present in the beam, a best-fit of the experimental data is obtained. A non-negligible reactivity from the spin-orbit excited $Cl(^2P_{1/2})$ atom is also found in recent studies by Liu and coworkers, using the Doppler selected TOF method, of the excitation function[5] and also of the differential cross section.

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Exploring the reaction dynamics of nitrogen atoms : A combined crossed beam and theoretical study of $N(^2D) + D_2 \rightarrow ND + D$

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Recently, detailed comparisons between integral and differential cross section measurements and exact quantum mechanical (QM) scattering calculations on *ab initio* potential energy surfaces (PESs) have been carried out for the benchmark three-atom reactions $H+H_2$, $F+H_2$, and $Cl+H_2$.[1] These are all direct, *abstraction*, collinearly dominated reactions which have no potential well on the minimum energy path. In an effort to provide experimental data for more complex reactions involving three-atoms, as *insertion* reactions which occur on PESs with a deep potential well between reactants and products, we have undertaken the study of the reaction[2]

$$N(^2D) + H_2\,(^1\Sigma^+) \rightarrow NH(X^3\Sigma^-) + H(^2S) \qquad \Delta H^\circ_0 = -33.2\ \text{kcal/mol} \qquad (1)$$

the simplest reaction of nitrogen atoms, of considerable fundamental and practical relevance. This reaction has recently attracted considerable experimental and theoretical interest, in particular it has become amenable to accurate theoretical treatments.

In the first successful reactive scattering study of nitrogen atoms, the angular and velocity distributions of the ND product from the isotopic variant reaction $N(^2D)+D_2$ at 5.1 and 3.8 kcal/mol collision energies have been obtained in a crossed molecular beam study with mass spectrometric detection. The center-of-mass product angular distribution is found to be nearly backward-forward symmetric, reflecting an insertion dynamics. About 30% of the total available energy goes into product translation, indicating a high internal excitation of the ND product, in agreement with the results of recent LIF studies.[3] The experimental results were compared with those of quasiclassical trajectory calculations on an accurate potential energy surface obtained from large scale *ab initio* electronic structure computations.[4] Good agreement was found between the experimental results and the theoretical predictions, although the calculated angular distributions are slightly backward biased (with respect to the N atom direction), especially at the lowest energy. Very recently, exact quantum scattering calculations have been performed for reaction (1).[5] This will allow in the near future to carry out accurate comparisons between experiment and theory also for an *insertion* reaction and to test unambiguously the *ab initio* PES of NH_2.

The comparison between the results for $N(^2D)+D_2$ with those obtained recently in our laboratory[6] at a comparable energy for the similar reaction $O(^1D)+D_2$ revealed to be very interesting. While only insertion is observed for $N(^2D)+D_2$, both insertion and an onset of abstraction are seen for $O(^1D)+D_2$.[7]

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Crossed Beam and Theoretical Studies of the Reactions of Nitrogen Atoms with Unsaturated Hydrocarbons : N(^{2}D) + C$_2$H$_2$ and C$_2$H$_4$

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Despite extensive investigation on the kinetics of nitrogen atom reactions, little is known about their reaction dynamics. We have recently measured, for the first time, product angular and velocity distributions for atomic nitrogen reactions in crossed beam experiments with mass spectrometric detection.[1,2] We exploit the capability to generate intense, continuous supersonic beams of N atoms by radio-frequency discharge in high pressure N$_2$/rare gas mixtures through a quartz nozzle. The beams are characterized by Stern-Gerlach magnetic analysis: 72% of the N atoms are found in the ground ^{4}S state, and 21% and 7% in the first excited ^{2}D and ^{2}P states (lying 2.39 eV and 3.56 eV, respectively, above the ground state).[3]

Here, we report on the investigation of the reaction dynamics of excited nitrogen atoms N(^{2}D) with unsaturated hydrocarbons, such as acetylene and ethylene, using the crossed molecular beam scattering technique with mass spectrometric detection. These reactions are significant in a wide variety of systems, in particular in the atmosphere of Saturn's moon Titan.[4] The reactions of N(^{4}S) with C$_2$H$_2$ and C$_2$H$_4$ are nearly thermoneutral and the very small rate constants (k$_{298}$~10^{-16} cc molec^{-1}s^{-1}) point to high activation energies. The reactions with N(^{2}D) are instead strongly exoergic and are expected to proceed with large cross section. The possible reactions of N(^{2}P) are expected to be slow on the basis of simple adiabatic electronic energy correlation diagrams.

From product angular and velocity distribution measurements at different collision energies (3-10 kcal/mol) we have found that the reaction N(^{2}D)+C$_2$H$_2$ leads to H+HCCN (cyanomethylene) formation ($\Delta H^0_0 \cong -55$ kcal/mol) and proceeds through a long-lived complex intermediate. The reaction channel leading to CCN + H$_2$, although somewhat more exoergic than HCCN + H, has not been observed to occur. The reaction dynamics are elucidated and the results discussed at the light of recent theoretical calculations[5] on the relevant potential energy surfaces.

From product angular and velocity distribution measurements at E$_C$=7.95 kcal/mol we have found that the reaction N(^{2}D)+C$_2$H$_4$ leads to H+C$_2$H$_3$N formation (in different isomeric forms: azirine, ketenimine, acetonitrile) via an osculating complex. Experiments at more collision energies are currently under way. The channel leading to H$_2$ elimination and cyanomethyl (CH$_2$CN) formation is not observed to occur. Again, the dynamics are elucidated and the results discussed at the light of recent theoretical calculations[6] on the relevant potential energy surfaces.

Experiments on other reactions, such as N(^{2}D)+methylacetylene and N(^{2}D)+benzene, are being planned.

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AUTOIONIZATION OF Ne*($^3P_{2,0}$)-CH3Cl COLLISIONAL COMPLEXES AT THERMAL ENERGIES

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Collisional autoionization processseses are commonly described through a complex potential, where the real part represents the effective interaction of the two colliding particles and the imaginary part represents the coupling with the ionization continuum [1]. Recent experimental results on ionization of simple molecules by rare gas metastable atoms have shown that anisotropy of both components of the complex potential (real and imaginary part) can strongly influence the energy dependence of total and partial ionization cross sections, that is cross sections for the total ion formation and for the population of different electronic states of the nascent ion [2]. Anisotropy effects have also been observed on specific features of the electron energy spectra as measured as a function of collision energy [3].

Based on previously measured cross sections for the production of specific ions, such as CH_3Cl^+, CH_3^+ and CH_2Cl^+, in Ne*($^3P_{2,0}$)-CH3Cl collisions, at energies between 0.05 and 0.3 eV [4], a study of possible anisotropy effects on ionization of methyl chloride has been carried out. A potential energy surface has been built up for the interaction of metastable neon atoms with methyl chloride by using recently developed semiempirical rules [5]. Then, within the framework of the electron transfer dynamics for ionization, the coupling with the continuum has been described through the electron density distribution of the orbitals involved in ionization. Following this model, the energy dependence of collisional autoionization cross sections have been computed using the quasiclassical trajectory method.

The results indicate that an increase of collisional energy corresponds to a modification of the branching for the population of different electronic states of the nascent CH_3Cl^- ions. Because of specific fragmentation of these ions, the cross section for the formation of each final product has been determined as a function of collisional energy and compared with the experimental results of ref.4. Analysis of the results allows us to establish that ionization occurs predominantly for specific geometries of the intermediate complex. In particular, the approach of neon metastable atoms to CH3Cl, towards the chlorine atom, leads mainly to CH_3Cl^+ and CH_3^+ ions, while the approach towards the the methyl group produces preferentially CH_2Cl^+ and CH_3^+ fragments.

Anisotropy effects can be studied directly through the measurement of the steric dependence of the opacity function of the system by using a beam of oriented CH3Cl molecules. This study is currently in progress [6].

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QUASICLASSICAL DYNAMICS AND STEREODYNAMICS OF THE $O(^1D) + HCl$ REACTION

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Abstract

A multiproperty analysis of the ground ($1^1A'$) potential energy surface (PES) for the $O(^1D) + HCl$ system is being carried out after improving the PES discussed in M.L. Hernández *et al.* (*J. Chem. Phys.* **1996**, *105*, 2710) by properly including the electronic excitation of the isolated oxygen atom. The analysis is based on the comparison of some scalar (such as branching ratios, translational and vibrational product distributions) and vector (angular distributions in the laboratory frame and other two- and three-vector correlations) properties of the products. These were calculated by running quasiclassical trajectories. Comparison is made with data obtained from the crossed beams experiment of Balucani *et. al.* (*Chem. Phys. Letters* **1991**, *180*, 34) and with laser induced fluorescence (C.R. Park and J.R. Wiesenfeld, *Chem. Phys. Letters* **1989**, *163*, 230) and Fourier transform spectroscopy (E.J. Kruus, B.I. Niefer and J.J. Sloan *et. al. J. Chem. Phys.* **1988**, *88*, 985) experiments. Good agreement was found for all the investigated properties including the inverted vibrational distribution of OH that was not possible to reproduce using the previous surface. Details about branching (both macroscopic and microscopic), scalar and vector distributions will be given at the Conference.

AN AB INITIO STUDY OF THE $O(^1D) + HBr$ REACTION

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Abstract

The lowest singlet $1^1A'$ and $1^1A''$ potential energy surfaces (PES) of the $O(^1D) + HBr$ system have been computed at *ab initio* level. The Complete Active Space SCF (CASSCF) method was used in most of the calculations, considering all the valence orbitals as active. Analytical gradient calculations using the CASSCF wavefunction were performed in order to localize the stationary points both in the $^1A'$ and $^1A''$ surfaces. Multi-Reference Configuration Interaction (MRCI) calculations were subsequently performed at selected nuclear geometries in order to improve the determination of the barrier heights and the energy balance. Since using all configurations in the CASSCF as references in the MRCI leads to prohibitively long CI expansions, a selection was required. An occupation was included in the reference space if the absolute value of the coefficient of one of its component spin couplings exceeded a threshold of 0.05. All the valence electrons were correlated. Zero point energy corrections were evaluated considering experimental frequencies for the equilibrium structures and computed frequencies at CASSCF level for saddle points. The basis set employed for the calculations is of double zeta plus polarization quality for all the atoms. Corrections were also introduced in other regions of the PES by properly scaling calculated values. Resulting electronic energy values for the ground and the first excited PES have been independently fitted by using expansions in bond order coordinates as in previous calculations for the $O(^1D) + HCl$ system (M.L. Hernández *et al.*, *J. Chem. Phys.* **1996**, *105*, 2710). Care was taken of the electronic O-atom excitation by smoothly modifying the long range potential of HBr in such a way that only the high HBr vibrational energy levels ($v \geq 7$) were affected. On the fitted surfaces quasiclassical trajectory calculations have been performed and compared to existing experimental data.

Reactive Quenching of Electronically Excited OH in Collisions with Molecular Hydrogen

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For 25 years, it has been known that electronically excited OH $A\ ^2\Sigma^+$ radicals undergo efficient nonradiative decay upon collisions with molecular partners. However, the products of this electronic quenching event have not been identified previously. This laboratory has recently demonstrated that reactive quenching, OH $A\ ^2\Sigma^+ + H_2 \rightarrow H + H_2O$, is a significant decay channel for OH $A\ ^2\Sigma^+$ in collisions with H_2. Doppler spectroscopy has been employed to characterize the translational energy distribution of the H atom products. A bimodal velocity distribution has been observed, which is characterized by translational temperatures of approximately 1000 K and 13000 K. The average translational energy of the products for the two channels accounts for 3% and 40% of the 4.72 eV of available energy. Conservation of energy dictates that H_2O is produced with a bimodal internal energy distribution, with corresponding average internal energies of 4.6 eV and 3.0 eV. The bimodal distribution originates from two different dynamical pathways through the conical intersection region that funnels OH $A\ ^2\Sigma^+ + H_2$ into $H + H_2O$. Analogous experiments conducted on OH $A\ ^2\Sigma^+ + D_2$ reveal that *both* D and H atoms are produced, consistent with two distinct pathways for this nonadiabatic chemical reaction.

Stereodynamic Control in OH-H$_2$

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The orientation of OH with respect to H$_2$ may be controlled to some extent by stabilizing the reactive partners in a weakly bound complex. Such OH-H$_2$ reactant complexes have been generated in this laboratory and characterized by vibrational spectroscopy. Vibrational activation supplies sufficient energy to initiate a reactive or inelastic half-collision event, in which the reagent approach geometry is restricted by the 'structure' of the complex. In order to interpret the experimental results, the relative orientation of the OH and H$_2$ partners within the complex must be determined. Fortunately, OH-H$_2$ has been the focus of high-quality *ab initio* calculations of the intermolecular potential energy surfaces and 4D quantum calculations of the bound states. We have evaluated the degree of orientation of the OH and H$_2$ diatoms within the complex from probability amplitudes ($|\Psi|^2$) computed for certain intermolecular states of OH-H$_2$. Although the OH-H$_2$ complex is loosely bound with large amplitude internal motions, the unquenched angular momentum associated with each diatom serves to orient the reactants with respect to the body-fixed frame. The relative orientation of the reactants is found to be strongly intermolecular state dependent, allowing the reagent approach geometry to be systematically manipulated. The restricted reagent approach geometry in vibrationally activated OH-H$_2$ complexes may influence the product state distributions for the inelastic scattering channel and may also have a strong effect on the branching between reactive and inelastic scattering channels.

ACHROMATIC LENSES FOR POLAR MOLECULES: FOCUSING FOR LOW AND HIGH FIELD SEEKING STATES

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For many years hexapoles have been used to focus symmetric top molecules. This focusing allows selection of molecular states that can be oriented in electric fields. Recently I presented[1] an analysis of the focusing of symmetric tops in hexapoles, and this analysis considered the effects of higher order Stark effects, hyperfine coupling, and hexapoles constructed from cylindrical rods instead of the ideal pole shape. These calculations represent the first comprehensive analysis of hexapole focusing, and the results clearly show the aberrations of hexapole lenses. Even to first order in the Stark effect, hexapoles have chromatic aberrations in that molecules with different velocities are focused at different positions. However when higher order Stark effects are considered, spherical aberration is also found, and these aberrations cause the focus position to depend on the angle from the hexapole axis at which the molecule enters the lens.

This paper presents important generalizations and extensions of the earlier work. Here I show that spherical and chromatic aberrations may be minimised for quadrupole,hexapole, and alternate gradient lenses. Consequently these corrected lenses may be used to provide excellent state selection, velocity selection, mass selection, and even nuclear spin state section for polar symmetric tops, asymmetric tops, and diatomic molecules in states whose energies either increase or decrease in an electric field. Hence effective focusing is now possible for states such as the $J=0, M=0$ state of a diatomic molecule, and not just the low field seeking states of symmetric top molecules. The lowest energy rotationl states of polar molecules are the easiest to orient by the brute force method, and it now appears that these states can be effectively selected with a electrostatic focusing lens.

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An improved potential energy surface for the C + NO reaction

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The gas phase reactions of atomic carbon with nitric oxide,

$$C(^3P) + NO(X^2\Pi) \xrightarrow{k_1} CN(X^2\Sigma^+) + O(^3P), \qquad (1)$$

$$C(^3P) + NO(X^2\Pi) \xrightarrow{k_2} CO(X^1\Sigma^+) + N(^2D), \qquad (2)$$
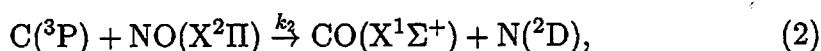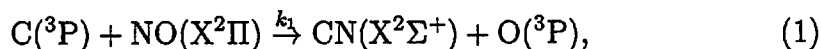
are important for the understanding of NO reburning, i.e., the conversion of nitric oxide to HCN and eventually N_2 using fuel as a reducing agent[1]. The reactions of NO with atomic carbon (and C_1 hydrocarbons like CH and CH_2) are especially important at high combustion temperatures[2].

A previously published potential energy surface for this system [3, 4] has been improved. New extensive ab initio calculations using CASPT2 have been performed for molecular geometries not considered in earlier work. A new analytical fit of the $^2A''$ surface is presented with special attention paid to the long-range behavior of the potential. Rate coefficients in a temperature range from 200 K to 4500 K have been obtained using classical trajectory calculations and are compared to experiment.

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Spin–orbit effects in quantum mechanical rate constant calculations for the F+H$_2$ → HF+H reaction

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Exact and approximate quantum mechanical reaction probabilities and cumulative reaction probabilities at selected values of the total angular mometum J have been performed for the F+H$_2$ reaction on the adiabatic Stark and Werner [1] and Hartke, Stark and Werner [2] (hereafter SW and HSW, respectively) potential energy surfaces (PES), the latter including spin–orbit corrections in the entrance channel. The approximate calculations are based on the Adiabatic Rotation Approximation (ARA). The cumulative reaction probabilities have been employed to obtain exact and approximate (ARA and J–shifting) thermal rate constants for the title reaction in the temperature range 220–700 K. The exact and approximate results on both PESs have been compared with experimental determinations [3] and previous theoretical predictions [4–6]. In particular, the comparison with recent reaction probability calculations based on the exact treatment of spin–orbit and Coriolis coupling for this system [6] demonstrates that the height of the adiabatic potential energy surfaces is too high, and that the participation to the rate constants from reaction with spin–orbit excited F(^{2}P$_{1/2}$) atoms through non–adiabatic channels is negligible.

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The dynamics of the O(^{1}D)+HD reaction studied by the quasi–classical trajectory surface hopping method on new *ab initio* potential energy surfaces. Simulation of Doppler–selected time–of–flight measurements

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Adiabatic quasi–classical trajectory (QCT) calculations for the O(^{1}D)+HD reaction on the new *ab initio* 1A' and 1A" potential energy surfaces (PES) by Dobbyn and Knowles [1] (hereafter DK) have been performed at the collision energy (0.196 eV) and reagent rotational temperature of the Doppler–selected time–of–flight experiments by Hsu and Liu [2]. The adiabatic calculations on the DK PESs has been compared with those carried out on the 1A' and 1A" K PESs [3,4]. The results obtained on the 1A' DK and K PESs are quite similar. However, the calculations on the 1A" DK and K PESs show interesting differences, both in the absolute values of the reaction cross section and in the product rotational distributions. Whereas the OH(v'=4,j') rotational distribution calculated on the 1A" K PESs shows a prominent bimodality, the distribution peaking at j'=1 and j'=13, the corresponding distribution calculated on the 1A" DK PES is monomodal and peaks at j'=6. In addition, the differential cross sections calculated on the 1A" DK PES are more sideways than the ones calculated on the 1A" K PES indicating a significant different dynamics. Non–adiabatic QCT calculations have been performed using the surface hopping methodology on the 1A' and 2A' DK PESs in a similar fashion as in the calculations reported by Schatz *et al.* for the O(^{1}D)+H$_2$ reaction on DIM PESs [5], and the results are very similar to those obtained adiabatically on the 1A' DK PES. The analysis of the trajectories starting on the 2A' PES shows a differential cross section with a significant forward peak (the forward direction being that of the incoming atom), but its relative contribution to the overall reactivity is much smaller than that of the trajectories starting on the 1A' PES. The adiabatic and non–adiabatic QCT calculations have been employed to simulate the experimental measurements for the title reaction reported by Hsu and Liu [2]. The experimental results are best reproduced when contribution to reaction from only the adiabatic 1A' K or DK PESs is considered. These results are in agreement with previous experimental/QCT predictions for the O(^{1}D)+H$_2$ reaction [6].

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The assessment of the H_3 *ab initio* potential energy surfaces. State–resolved differential cross sections *versus* thermal rate constants

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The dynamics of hydrogen exchange reaction in its $H+D_2 \rightarrow HD(v', j')+D$ isotopic variant has been investigated theoretically by means of exact quantum mechanical (QM) and quasi–classical trajectory (QCT) calculations at collision energies ranging from 0.53 eV up to 2.67 eV. A detailed comparison of v', j' state–resolved QM differential cross sections (DCS) and state–to–state molecular beam experiments [1] has allowed a direct assessment of the quality of the different *ab initio* potential energy surfaces used in the calculations, and strongly favours the newly refined version of the Boothroyd–Keogh–Martin–Peterson (BKMP2) surface [2]. The differences observed in the calculations on the various PESs are related to their different topology [1]. Although the comparison of accurate QM low temperature rate constants [3,4] and the existing experimental data for the $D+H_2$ reaction suggest that better agreement is obtained with calculations carried out on previous, less accurate, PESs, new QM rate constant calculations for the $H+D_2$ reaction [5] on the BKMP2 PES show an almost perfect accordance with the available measurements. This calculations suggest that more refined rate constant measurements at low temperatures for the different isotopic variants of this prototypic reaction would be very timely.

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Low temperature rotational relaxation of N_2 and N_2–He,Ne,Ar mixtures in free jets studied by resonance enhanced multiphoton ionization

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The rotational relaxation of N_2 in pure free jet expansions [1] and in mixtures with He, Ne and Ar has been investigated using a combination of resonance–enhanced multiphoton ionization (REMPI) and supersonic beam time–of–flight techniques. For pure N_2 and from the terminal rotational temperatures measured (see Figure 1), the average relaxation cross section has been estimated over a wide range of temperatures extending down to ≈ 5 K. The average cross section shows a maximum value of 50–60Å^2 at 20–30 K and decreases at about 30Å^2 at the lowest temperatures measured [1]. At temperatures higher than 30 K, the cross section decreases slowly with increasing temperature and converges to the available theoretical estimations. The results are compared to previous measurements obtained using different techniques and, in some cases, significant discrepancies are found. For the N_2–He,Ne,Ar mixtures, similar measurements have been performed and the results will be presented and discussed at the conference.
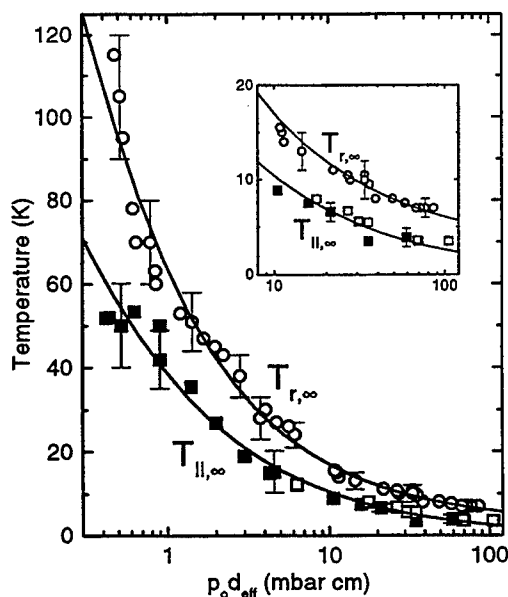
Figure 1: Measured terminal rotational (squares) and paralell translational (circles) temperatures as a function of $p_0 d_{\text{eff}}$ for pure N_2. Solid lines are best–fit model curves.

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Quasi–classical trajectory study of the Cl+H_2,D_2,HD reactions: cross sections and rate constants

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Quasi–classical trajectory (QCT) calculations of cross sections and rate constants have been performed for the Cl+H_2, Cl+D_2 and Cl+HD→HCl(DCl)+D(H) reactions on a new potential energy surface (PES) by the group of Werner [1] (hereafter BW). The results have been compared with previous QCT calculations [2,3] on the G3 PES [4] and with recent experimental data by the group of Liu [5,6]. It has been found that reagent rotation enhances the reactivity in calculations for the Cl+H_2(D_2) reactions on the BW PES in accordance with the latest experimental results [5]. In addition, the QCT results for the Cl+HD(v=0,j=0,1) reaction on the BW PES predict an intramolecular branching ratio Γ(HCl/DCl)≪1, also in very good agreement with experiment [6]. These results are in strong contrast with those obtained on the G3 PES [2,3], where larger thresholds and smaller cross sections were found as reagent rotation increases, as well as a branching ratios Γ(HCl/DCl)>1 for the Cl+HD reaction. QCT calculations have also been performed for the Cl+HD(v=1,j=1,2) on both the G3 and BW PESs and the results, which will be presented and discussed at the conference, have been compared with recent experimental measurements by the group of Zare using the "photoloc" technique [7].

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Hyperspherical and related coordinates for tetratomic and polyatomic systems

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Four-atom systems are currently under the focus of state-to-state reactive scattering calculations as an extension of activity on three-atomic systems toward the dynamical treatment of polyatomic molecules. Understanding body frames and their singularities [1] will be an important part of this effort. We do this by introduction of symmetric hyperspherical coordinates [2] which easily permits separation of internal configuration space (Eckart frames).

This space is spanned by the hyperradius ρ and two angular variables, which are related to inertia moments, and by three kinematic angles [3].

For internal dynamics we adopt a general model which decouples kinematic angles and suggests working only with kinematic invariants by adding different kinematic angles case by case [4]. In this analysis kinematic rotations [5] are a very important tool. The model also provides a reasonable reduced-dimension approach for certain symmetry conserving processes (e.g. ammonia inversion problem). Suitable expansion basis sets can be obtained by representing the eigenfunctions for kinetic energy in hyperspherical harmonics.

A geometrical and group-theoretical analysis of symmetry properties of eigenvalues and eigenfunctions is carried out to develop such type of expansion basis sets for the scattering wavefunction and thus the implementation for extensive numerical calculations.

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Fitting of potential energy surfaces by discrete polynomials.

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Classical orthogonal polynomials of discrete variable have turned out to be very useful to fit functions represented in tabular form thanks to the possibility of avoiding laborious numerical integration required by the use of polynomials of continuous argument (see ref.1). A relevant role is played by Hahn polynomials (ref. 2), discrete analogues of Jacobi polynomials, which can be related to the Wigner's 3j symbols, establishing a significant correspondence between the algebra of these polynomials and that of angular momentum vector coupling coefficients (ref. 3). An examination of their asymptotic behaviour has accounted for the role of these polynomials as discrete analogues of hyperspherical harmonics. This asymptotic correspondence has been exploited in the recently developed hyperquantization algorithm, which has turned out to be very efficient for the solution of some computational problems which emerge in the quantum treatment of elementary reaction dynamics. The aim of our present work is to explore the potentialities of Hahn polynomials for the accurate fitting of potential energy surfaces. Such a versatile type of polynomials has been in fact successfully employed as an orthogonal basis set for the expansion of potential energy surfaces with a very high level of accuracy.

The method described has been tested on the Henon-Heiles potential, which we consider in this application a model for bidimensional functions. The value of Henon-Heiles potential is reproduced exactly at the grid points and an excellent agreement with interpolated values is obtained, both for uniform and non-uniform grids. This method has been then applied for the fitting of the potential energy surface of malonaldehyde, a prototype system for both theoretical and experimental studies of the dynamics of intramolecular proton transfer processes. Ab initio points were calculated by C. Adamo and V. Barone. The potential function has been expanded in terms of the Hahn polynomials on a grid of symmetric hyperspherical coordinates at fixed values of the hyperradius.

In conclusion, we believe that the combination of this new method for fitting potential energy surfaces with a proper choice of the grid of ab initio points could be a useful tool for the study of the dynamics of chemical processes.

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Ab-initio PES and hyperquantization dynamics: quantum mechanical reactive cross sections for the He + H_2^+ system

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Within the framework of the hyperspherical approach to reaction dynamics, we have developed and implemented a new method, that we have called *hyperquantization algorithm*[1] to solve exactly the quantum mechanical three-atom reactive scattering problem. The most important ingredients of this algorithm are generalized $3j$ symbols or Hahn Polynomials[2] which are the discrete analogs of hyperspherical harmonics on a grid of points. The use of sequential diagonalization-truncation tecniques[3] to diagonalize the Hamiltonian matrix makes this method very efficient[4] and competitive with respect to the existing ones.

Calculations of state-to-state reactive cross sections for the reaction He + H_2^+ → HeH^+ + H on new ab-initio potential energy surfaces will be presented. The sensibilty of the dynamical quantities to different analytical fitting and to different criteria for the choice of the ab-intitio points in the configurations space is studied. In particular the dynamical effects of the resonances in this system is investigated with exact and a ccurate approximated[5] methods.

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Empirical Potential Energy Surfaces including spin-orbit effects for F + H$_2$ system and multisurface dynamics theory by hyperquantization

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The interaction potentials between the open-shell fluorine atom (^{2}P) and the hydrogen molecule H$_2$ treated as a rigid rotor have been investigated by inelastic scattering measurements carried out in our research laboratory[1]. The long range part of the interaction was characterized with high accuracy. Therefore the elements of the electrostatic matrix can be explicitely set out on an asymptotic p-orbitals basis of the F atom, and are directly related to the expression of the three adiabatic PESs ($1\,^2$A', $2\,^2$A' and ^{2}A") involved in the system.

Such a result, joined with the knowledge of the full ground-state surface from ab initio calculations, allows us to develop a complete theory for the reaction dynamics on the three coupled electronic states. Under this approach, the total angular momentum exibiths contributions from both nuclear and electronic motion, so that, owing to the electronic spin, possible values of the total angular momentum J are half-integer. The treatment of the simplest case J = 1/2 imposes the consideration of values of the nuclear total angular momentum different from zero.

An exact partition of the Hamiltonian devoted to simplify spin-orbit, rotational and Coriolis coupling terms is proposed, and the hyperquantization technique [2,3] is shown to be physically motivated as well as computationally effective for the inclusion on the reaction dynamics of specific interactions among ground and excited electronic states in the regions of the configurations space where these effects play a significant role.

Projection of the scattering eigenfunctions on the reactant and product rovibronic asymptotyc states is also discussed.

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Molecular beam reaction dynamics of B(^{2}P$_j$) with simple unsaturated hydrocarbons

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Reactions of boron atoms with simple unsaturated hydrocarbons are prototype reactions leading to the formation of hydrogen deficient molecules in the organo H-C-B system. Especially the chemical dynamics in the reaction of atomic boron, B(^{2}Pj), with acetylene, C_2H_2 ($X^1\Sigma_g^+$), are of potential importance in the metal catalyzed acetylene - vinylidene conversion; the involved reaction intermediates and reaction are of fundamental significance in hetero atom organic chemistry. Finally, the laboratory gas phase synthesis and identification of simple organo boron compounds could lead to an identification of these species in extraterrestrial environments like cold, interstellar molecular clouds - a natural 'laboratory' where a huge number of highly unstable radicals have observed. Despite these important applications, few atomic boron reactions have been investigated so far and only in matrix isolation studies; no gas phase studies are available.

Here we report on the first experimental 'gas-phase' investigation of the reactions of atomic boron with the simplest unsaturated hydrocarbons, C_2H_2 and C_2H_4, by means of the crossed molecular beam technique with mass spectrometric detection. In our crossed beam experiments, a supersonic beam of boron atoms was generated by laser ablation of a boron rod at 266 nm and seeding the ablated atoms in helium carrier gas. Information on the reaction dynamics was extracted from the time-of-flight spectra and the laboratory angular distribution by using a forward-convolution technique.

Data analyses are still in progress. The derived preliminary center-of-mass functions, combined with high level electronic structure calculations, suggest that the B atom interacts with the π electron density in both cases[1]. In the case of the reaction with acetylene, two channels are possible leading to a bend B-C-C skeleton or to a cyclic B-C_2H_2 intermediate. The reaction dynamics of the first channel is governed by a H atom migration to form the HBCCH complex, which subsequently fragments to the linear HBCC isomer and a H atom. The assignment of the second, most probable cyclic product isomer is still in progress.

In the case of the reaction with ethylene, the B atom attacks the π electron density of the ethylene molecule forming a hetero tricycle. A successive H atom migration from a carbon to the boron atom takes place prior to a C-H bond rupture, yielding a H atom and the **borirene** molecule. This is the first clean gas phase synthesis of the simplest, closed shell hetero atomic, 2 π aromatic system. We recall that, ever since the formulation of the aromaticity concept, the synthesis of small, 2π aromatic molecules such as c-C_3H_2 and $C_3H_3^+$ has been a challenge to organic chemists. No gas phase synthesis of hetero cyclic aromatic 2π systems was reported so far, as these molecules are extremely reactive and thermally unstable. The simplest boron hetero cyclic aromatic system, borirene, c-BC_2H_3, was previously detected only in matrix isolation studies[2].

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Crossed Beam Studies of the Reactions of Nitrogen Atoms with Saturated Hydrocarbons : N(^{2}D) + CH$_4$

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The reactions of atomic nitrogen in the electronic ground state N(^{4}S) or excited state N(^{2}D) are very important in interstellar, combustion and atmospheric chemistries. In our laboratory, we have recently undertaken the investigation of the reaction dynamics of excited nitrogen atoms N(^{2}D) with both saturated and unsaturated hydrocarbons, such as methane, ethane, acetylene, ethylene, etc. using the crossed molecular beam scattering technique with mass spectrometric detection.[1-3] These reactions are significant in a wide variety of systems, in particular in the atmosphere of Saturn's moon Titan, where CH$_4$ is the most abundant hydrocarbon, followed by C$_2$H$_2$, C$_2$H$_4$ and C$_2$H$_6$.[4] We exploit the capability to generate continuous supersonic beams of N atoms by radio-frequency discharge in high pressure N$_2$/rare gas mixtures through a quartz nozzle. The beams are characterized by Stern-Gerlach magnetic analysis: 72% of the N atoms are found in the ground ^{4}S state, and 21% and 7% in the first excited ^{2}D and ^{2}P states (lying 2.39 eV and 3.56 eV, respectively, above the ground state).[5] The reactions of N(^{4}S) with hydrocarbons are either endoergic or have high barriers, while the reactions of N(^{2}P) are much slower than those of N(^{2}D).[6]

The reaction N(^{2}D)+CH$_4$, perhaps the most important reaction of N atoms in Titan's atmosphere, has recently attracted a great deal of attention. The rate constant at room temperature has been determined to be ~4×10^{-12} cm^3 molecule^{-1} s^{-1} and the activation energy ~1 kcal/mol.[6] Umemoto and coworkers[7] have carried out a detailed pump-probe laser-induced-fluorescence study of the reaction: both NH radicals and H atoms were detected as reaction products. The absolute yields for the H + CH$_2$NH and NH + CH$_3$ channels were found to be 0.8±0.2 and 0.3±0.1. *Ab initio* molecular orbital calculations have been carried out on the N(^{2}D)+CH$_4$ reaction (stationary points, energetics, barrier heights, products), which suggest that N(^{2}D) inserts into the C-H bond of CH$_4$.[8]

We have investigated in detail the chemical dynamics of the dominant H-displacement channel in the N(^{2}D)+CH$_4$ reaction. From product angular and velocity distribution measurements at six different collision energies (ranging from about 5 kcal/mol to about 15 kcal/mol) we have elucidated the dynamics of pathways leading, via a CH$_3$NH intermediate, to formation of H+CH$_2$NH, H+CHNH$_2$ and possibly H+CH$_3$N:

$$
\begin{aligned}
\text{N}(^2\text{D}) + \text{CH}_4 \quad &\rightarrow \text{H} + \text{CH}_2\text{NH} \qquad &\Delta\text{H}^\circ_0 = -73.6 \text{ kcal/mol} \\
&\rightarrow \text{H} + \text{CHNH}_2 \qquad &\Delta\text{H}^\circ_0 = -36.1 \text{ kcal/mol} \\
&\rightarrow \text{H} + \text{CH}_3\text{N} \qquad &\Delta\text{H}^\circ_0 = -19.9 \text{ kcal/mol}
\end{aligned}
$$
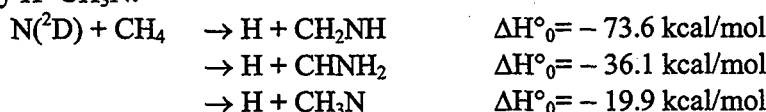
The results are discussed at the light of recent theoretical calculations on the relevant potential energy surfaces.[8]

Experiments on other reactions with saturated hydrocarbons, such as N(^{2}D)+C$_2$H$_6$, as well as with inorganic molecules as H$_2$O, are being planned.

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Predissociation dynamics of van der Waals complexes

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We have studied by high resolution electronic spectroscopy the allowed $S_1 \leftarrow S_0$ vibronic bands of the aniline-neon van der Waals complex from the 0_0^0 origin transition up to a vibrational excitation of 1300 cm^{-1} in the S_1 state.[1, 2] We obtained an extremely detailed picture of the properties of the S_1 vibrationally excited levels. From our rotationally resolved experiments we were able to measure the frequency of the band center and the homogeneous linewidth of the transitions; with the full assignment of the spectra it was also possible to determine the ground and upper state rotational constants. The combined analysis of these quantities give us the possibility to learn about the predissociation dynamics in these excited states and to probe the presence of promoting modes for this process. Ab initio quantum calculations were useful to understand the nature of the interactions responsible for the existence of promoting modes. The special role of the out-of-plane large amplitude motions was clearly revealed.

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IONIZATION OF AMMONIA MOLECULES BY COLLISION WITH METASTABLE NEON ATOMS

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The ionization of ammonia molecules by collision with metastable neon atoms (Penning ionization) has been studied by measuring the energy spectrum of emitted electrons and the mass spectrum of product ions [1], in a joined study between two laboratories.

In a crossed beam apparatus in Brest [2], the energy spectrum of the emitted electrons has been measured at an average collision energy of 0.045 eV . It has been found that primary NH_3^+ ions are produced in two electronic states: the ground state $NH_3^+(X^2A')$ and the first excited $NH_3^+(A^2E)$. In an other crossed beam apparatus in Perugia [3], a mass spectrometric study has been undertaken which revealed that, at the same collision energy, NH_3^+ and NH_2^+ final ions are produced. Absolute total ionization cross sections and branching fractions NH_2^+/NH_3^+ have been measured as a function of collision energy in the 0.03-0.2 eV energy range .

The mass spectrum compared with that of NeI photoionization, obtained in the same experimental conditions, shows that the NH_2^+/NH_3^+ branching fraction is remarkably lower in Penning ionization. This indicates that the particle interaction strongly influence the collisional autoionization dynamics. Total ionization cross section is high (~57 $Å^2$ at 0.05 eV) and shows a decreasing energy dependence typical of systems characterized by a strongly attractive interaction.

From photoionization studies performed in various laboratories, it is well known that $NH_3^+(X^2A')$ ions primarily produced remain stable, while $NH_3^+(A^2E)$ give rise to an almost complete ($\approx 80\%$) dissociation to $NH_2^+ + H$. It is therefore possible to relate the electronic states of the primary ions to the final ionic products.

The NH_2^+/NH_3^+ branching fraction shows a weak but significant increase at higher collision energy. This is a consequence of a relative increase of population of the $NH_3^+(A^2E)$ electronic state. This observation can be explained by the increase of total energy and by a model which takes into account the interaction potential anisotropy combined with the electron density distribution of the orbitals involved in the ionization [4,5].

Analogies are present with the omologous $He^*(^3S)-NH_3$ collisional autoionization [6].

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Crossed Beam Studies of the Reaction Dynamics of $C(^1D)+H_2$ and $C(^1D)+CH_4$

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Atomic carbon is an important reactive species whose relevance ranges from combustion and hydrocarbon synthesis to interstellar chemistry. Despite their fundamental and practical importance, comparatively little is known (with respect to oxygen atoms for instance) about the reaction dynamics of carbon atoms, both in the ground state $C(^3P)$ and in the first electronically excited state $C(^1D)$ (located 1.263 eV above the ground state) under single collision conditions. In particular, crossed molecular beam (CMB) studies with mass spectrometric detection have become feasible only recently using *pulsed* beams of C atoms obtained by laser ablation of graphite.[1] However, for CMB studies using a "universal" detector, *continuous* beams are desirable for duty cycle reasons.[2]

Very recently, we have developed a radio-frequency discharge beam source able to produce *continuous* supersonic beams of carbon atoms $C(^3P,^1D)$ (containing only a few percent of C_2 and no C_3), starting from CO_2/rare gas mixtures. This development permits us to carry out readily product angular and velocity distributions for a variety of $C(^3P,^1D)$ atom reactions. While for reactions which are exoergic for both electronic states, the triplet and singlet contributions can be disentangled in angular and velocity distribution measurements (at least in favorable cases), for reactions which are endoergic for $C(^3P)$ it is possible to study cleanly the $C(^1D)$ reaction dynamics.

Here, we report on the first study, by the crossed molecular beam scattering technique with mass spectrometric detection, of the reaction dynamics of $C(^1D)+H_2$ and $C(^1D)+CH_4$ (we recall that the reaction of $C(^3P)$ with H_2 is strongly endoergic and that with CH_4 has a very high energy barrier). These reactions are of great fundamental and practical interest. While LIF studies of $C(^1D)+H_2$ have been reported,[3] no dynamical studies are available for $C(^1D)+CH_4$. Interestingly, the "chemical activation" of methane by carbon atoms leading to an excited ethylene molecule which undergoes "unimolecular" decomposition can be compared with the results of ethylene pyrolysis and of extensive studies, both experimental and theoretical, of ethylene photodissociation, most notably carried out very recently in Y. T. Lee's laboratory.[4] From product angular and velocity distributions we have obtained information on the relevant reaction dynamics.

The reaction $C(^1D)+H_2$ at a collision energy of 3.8 kcal/mol is found to proceed by *insertion* forming an excited CH_2 (methylene) radical which decomposes into H + CH (methylidene). The $CH(X^2\Pi)$ product is formed mainly in v'=0 and for a few percent also in v'=1. The mechanism and the product energy partitioning into translation, vibration and rotation are characterized. Experiments at a lower energy at which only CH(v'=0) is energetically accessible are under way.

The reaction $C(^1D)+CH_4$ at a collision energy of 7.2 kcal/mol proceeds by insertion forming an excited ethylene/ethylidene molecule which decomposes following two energetically and dynamically quite different reaction pathways: simple bond fission leads to H + CH_2CH (vinyl) and concerted elimination to H_2 + acetylene. The center-of-mass angular and translational energy distributions for each reaction channel are derived. Interesting comparisons are made between the dissociation behavior of the $[C_2H_4]^*$ reaction intermediate and the UV photodissociation of the C_2H_4 molecule at comparable total energy.

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Time-Resolved Internal Conversion

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Resulting from electronic excitation, the primary processes of radiationless energy redistribution in polyatomic molecules are known to play an important rule in molecular geometry changes leading ultimately to chemical reaction. The resolution of these first steps is a central yet complex problem, especially for the internal conversion where the difficulty is to separate electronic coupling and intramolecular vibrational energy redistribution (IVR). Here, we report a general method to observe any modification of interaction configuration through time-resolved photoelectron spectroscopy (TRPES). Its demonstration has been done by resolving the internal conversion of a long linear polyene: all-trans decatetraene ($C_{10}H_{14}$). A wavepacket, that is prepared by a femtosecond laser pulse, evolves in excited electronic states before to be projected by a second femtosecond laser pulse into the ionization continuum which the electronic structure is used as template for revealing electronic coupling. Partial ionization cross-sections may differ drastically with the molecular orbital nature of the excited electronic states, favouring the two photon-ionization relative to the one-photon ionization. As the non-adiabatic coupling proceeds, the changing electronic character of the wavepacket alters ionization cross-sections leading to large shift of photoelectron spectrum. Consequently, TRPES gives a molecular dynamics insight with the ability to distinguish the purely electronic coupling from the nuclear dynamics such as IVR.

Infrared Spectra During and After IR-Multiphoton Excitation Measured by Time Resolved FTIR Spectroscopy of CF_2HCl, CF_3I and $(HCOOH)_2$

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Multiphoton excitation with intense infrared laser pulses is one of the most interesting techniques to study primary processes of intramolecular energy transfer, isotope selective, and possibly mode selective reactions [1-3]. In this context the internal state distribution of reactants and products during and after excitation is of particular interest. The complete internal and translational state population distribution of gas phase molecules can, in principle, be determined from IR-spectra, measured with sufficiently high resolution. Therefore, applying time resolved techniques, the population distribution during and after laser excitation can be derived. We have recently shown that MHz resolution IR-diode laser spectroscopy can be used even to derive hyperfine distributions in addition to rovibrational distributions [4-7]. With step scan FTIR techniques a time resolution of 5-10 ns is possible and the experimental technique has been recently applied to study the photochemically initiated reaction dynamics of bacteriorhodopsin [8] and the energy transfer from vibrationally highly excited NO_2 [9]. The experimentally accessible time resolution is significantly shorter than typical pulse lengths from a TEA-CO_2 laser, widely used in IR-multiphoton excitation experiments. This renders it possible to investigate the time evolution and population distribution of molecules during and after IR-multiphoton excitation under essentially collision free conditions. A detailed knowledge of the IR-spectra of highly excited molecules is necessary to improve the sensitivity of IRLAPS experiments [10,11] and the selectivity in isotope separation [2]. We have applied time resolved FTIR techniques to investigate the time evolution of IR-spectra during IR-multiphton excitation over a broad spectral range to determine the time dependence of the total concentration and the population distribution of reactant and product molecules.

For CF_2HCl the changes of the IR-spectra of the CH-stretching vibration after the IR-multiphoton excitation have been measured. CF_3I is dissociated efficiently by the pulsed CO_2 laser radiation and in addition to the time evolution of the IR-spectra for the symmetric (a_1) CF_3-stretching vibration around 1075 cm^{-1} and the degenerate (e) CF_3-stretching vibration around 1180 cm^{-1} the time dependent absorption spectrum of the CF_3 reaction product around 1250 cm^{-1} could be detected. Only seven CO_2 laser photons are necessary to dissociate $(HCOOH)_2$ into two monomers. During the exciting CO_2 laser pulse the absorption spectrum of the CO-stretching vibration of formic acid dimer around 1220 cm^{-1} is shifted signifiantly to lower wavenumbers and the absorption of the CO-stretching vibration of the monomer around 1105 cm^{-1} increases due to the dissociation of the dimer. We have also observed the OH-stretching vibration, providing indication of non H-bonded OH and perhaps of a two step mechanism for dissociation.

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Energy dependence and threshold energies for $Li + FH$ and its isotopic variants.

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Due to the peculiar height and location of the transition state on the potential energy surface adopted, the $Li + FH$ reaction leads to interesting effects on the energy dependence of the reaction probability and of its threshold energy as H is changed into its isotopes.

To investigate in detail this feature of the $Li + FX$ ($X = H, D, T$) reactions exact quantum dynamical studies were performed using the APH3D computational procedure based on the APH coordinates formalism [1] [2].

To reconduct computing time into reasonable limits a parallel version [3] of the two main programs of APH3D was implemented on a Cray T3E. This allowed an extended investigation of the dependence of the reaction probability on the total energy. Sets of 63 energies were run for energies ranging from threshold to 0.6 eV. To obtain a more detailed information on the isotope effects, an energy step of $\Delta E = 5 \times 10^{-4} eV$ was used in the threshold region.

The calculations indicate that:

- translational energy at threshold is zero for $Li + FH$ ($v = j = 0$) and 4.40×10^{-2} and 7.16×10^{-2} eV for its D and T isotopomers, respectively;

- the background structure of the probability moves to higher energy when the mass of the exchanged atom is increased, in analogy with what occurs when the F atom is substituted by a heavier atom;

- resonances tends to smooth down for heavier atoms.

A serial version of the code was also run for values of the total angular momentum (J) grater than 0. In particular, we have calculated the $Li + FH$ reaction probability as a function of j and j' for $J = 2$ (both parities) at a total energy value of 0.294 eV. All the distributions show a unimodal behaviour with a maximum at $j = 2$. Such a maximum rises as a function of j' reaching its highest value at $j' = 6$.

Plots of the probability as a function of j' show also that, for $j = 2$, the reactivity decreases as l goes from 0 to 2 and then increases when $l = 4$ (only the even values of l are allowed).

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Exit-channel effects in three-atom unimolecular reactions : Towards their inclusion into Transition State Theory

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The study of the validity of transition state theory (TST) and its parents (RRKM, PST, SACM) is a very active field of research. This is mainly due to the large development of experimental techniques which make possible the extraction of detailed informations on a chemical reaction at the microscopic level and as a consequence, a severe test of TST.[1]

One of the main limitations of TST is its inability to accurately describe product state distributions in the general case. As a matter of fact, TST does not take into account the exit channel effects which alter the energy partitioning from the TS — where the predictions of TST are usually reasonable — to the separated products. For a three-atom unimolecular reaction, these effects are mainly coupling between rotational and translational motions of the nascent products.

A theoretical study of exit channel effects is presented within the framework of classical mechanics. Moreover, a simple model is proposed to mimic these effects. Inclusion of this model into TST extends in some cases its applicability to the description of product state distributions.[2]

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Nonlinear Intensity Dependence in the Infrared Multiphoton Excitation and Dissociation of Methanol Preexcited to Different Energies

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IRLAPS (Infrared Laser Assisted Photofragment Spectroscopy) is a very sensitive technique to investigate vibrational overtone spectra of polyatmic molecules [1-3]. Usually a three step mechanism is applied: The molecules are selectively excited to the vibrational overtone under consideration by a single near-IR laser photon. The preexcited molecules are then dissociated through multiphoton absorption of CO_2 laser photons in a second excitation step. The reaction products are finally detected by laser induced fluorescence (LIF). The sensitivity of the IRLAPS technique is in part determined by the selectivity of the IR multiphoton excitation step, where the dissociation of the relative small number of preexcited molecules has to be discriminated against molecules, dissociated from the vibrational ground state. The selectivity of the multiphoton excitation step can be improved significantly, if nonlinear intensity effects are properly taken into consideration for the experiments. Most molecules of moderate size (4-6 atoms) show a pronounced nonlinear intensity dependence for the IR-multiphoton excitation from the vibrational ground state due to their relatively low density of vibrational states for the first excitation steps [4-7]. For molecules preexcited to higher vibrational states this nonlinear intensity effect is absent, or reduced significantly. Thus applying low intensity, smooth CO_2 laser pulses will increase considerably the sensitivity of the IR-multiphoton excitation step in IRLAPS experiments.

In our experiments we have measured the fluence dependence of the IR-multiphoton dissociation of product yields for CH_3OH from the vibrational ground state and preexcited to $v_{OH} = 1,3$, and 5 with two different CO_2 laser pulses. For the dissociation from the vibrational ground state and from $v_{OH} = 1$ a pronounced higher dissociation yield has been determined for quasi mode-locked laser pulses from the free running laser compared to the dissociation yields from smooth single mode pulses. For molecules preexcited to $v_{OH} = 3$ and 5 the same dissociation yields have been measured for both laser pulses. The experimental results have been confirmed by model calculations based on a case B/C master equation including corrections to account for nonlinear intensity effects [4-8].

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An accurate *ab initio* double-valued potential energy surface including long-range interactions for the H_2O molecule

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Although there have been a lot of recent studies on the potential energy surface for the $\tilde{X}^1A_1$ ground state of the H_2O molecule [1–5], there is a lack of studies on the long range interactions on this system.

In the absence of those studies and mainly interested on the rovibrational spectra of water, the published potential energy surfaces don't reproduce the long range interactions or use a simplified form to emulate them neglecting "the intramolecular dependence of the atom-diatom dispersion coefficients" and the electrostatic quadrupole-quadrupole interaction between the O-atom and the H_2 diatom.

In contrast with this situation, the $O(^1D) + H_2(^1\Sigma_g^+) \rightarrow OH(^2\Pi) + H(^2S)$ reaction, which occurs mainly in this system, is believed to have a null activation barrier. So, the long range forces between the O atom and the H_2 diatomic should play an important role [6] on the dynamics of this important reaction in atmospheric and combustion chemistry. Despite that, this has been ignored in recent theoretical studies for this reaction [1, 6, 7].

In order to obtain an accurate potential energy surface covering all configurational space, we have semi-empirically modeled the long-range interactions and fitted a double-valued functional form to the best *ab initio* published data.

To represent the long-range interactions, we have done MCSCF *ab initio* calculations of the dipole and quadrupole charge distributions, as well as for the dipole polarizabilities. Those calculations have been made for the different atoms and diatoms in their ground and first excited state as they appear as fragments on the water dissociation on a double-valued potential energy surface [8]. In particular, we studied the (^3P) and (^1D) states of the O atom, the $(^2\Pi)$ and $(^2\Sigma)$ states of OH, and the $(^1\Sigma_g^+)$ and $(^3\Sigma_u^-)$ states of H_2. Using those results we have been able to semi-empirically model the electrostatic, induction and dispersion energies that arises on this system when any of its components is far apart from the others [9].

Using these long-range energy terms and accurate diatomic potential energy functions, the complete potential energy surface has been obtained fitting the total *ab initio* energies [4, 10, 11] to a double-valued functional form. The two diabatic surfaces are represented using the Double Many Body Expansion model (DMBE) [12] and the crossing term is represented using has a three-body energy function.

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TIME RESOLVED FOURIER TRANSFORM INFRARED EMISSION STUDIES OF CF$_3$ FORMED FROM THE UV PHOTOLYSIS OF CF$_3$I

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Time Resolved Fourier Transform Infrared Emission is a powerful technique when applied to the products of a photodissociation or chemical reaction, in that more than one species, and more than one quantum state of each species, can be observed simultaneously. It can be used for kinetic studies of photodissociation dynamics, chemical reactions and energy transfer processes, and for the measurement of product branching ratios and internal state distributions. In this contribution we describe studies of the CF$_3$ radical.

Infrared emission at 1185 and 1250cm^{-1} has been observed following the UV photolysis of CF$_3$I, and these features are assigned to vibrationally excited CF$_3$I and CF$_3$ respectively. Vibrationally excited CF$_3$ is produced in the 248nm photolysis of CF$_3$I, and strong emission from $\Delta v_3 = -1$ is seen, presumably in conjunction with excitation in the v_1 and v_2 modes as measured in a number of previous studies. Information on the nascent vibrational distribution of the CF$_3$ radical and subsequent energy transfer processes, such as to CF$_3$I itself, can be gained from the TR-FTIR technique.

In the presence of NO$_2$ further emitting species can be seen following the photolysis pulse; photodissociation of NO$_2$ itself is seen to give vibrationally excited NO, and vibrationally excited products of the CF$_3$ + NO$_2$ reaction are observed. Several groups have studied this reaction but, while the rate constant is reasonably well known there is some disagreement as to the mechanism and product branching ratios. Previous work in this group tentatively assigned emission features near 1850 and 1940cm^{-1} as from products FNO and CF$_2$O and the possibility of emission from an isomeric FON species at 1880cm^{-1} was discussed. Better quality spectra are now available and analysis of such spectra enables us to draw clearer conclusions as to the nature of the emitting species. We will also present a kinetic study of the CF$_2$O emission seen following the CF$_3$ + NO$_2$ reaction showing evidence of a third body process leading to the stabilised adduct CF$_3$NO$_2$.

A Dynamic and Kinetic study of N-N$_2$ collision processes

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In this work we present a study of the interaction of Nitrogen atoms and molecules; this is of interest for a kinetic description of non-equilibrium flows in air. In rarefied flows or when fast chemical reactions play a role the continuum assumption for the flow breaks down; more over the non-equilibrium can be so strong that even the assumption of translational equilibrium begins to fail. We then have to resort to a study of the complete Boltzmann equation. This issue can be addressed by the Direct Simulation Monte Carlo (or DSMC) technique [1]. We have developed a DSMC code with a state to state approach to the vibrational kinetics that generalises naturally the Master Equation approach by suggesting the possibility of a unified approach, where non equilibrium distributions for both translational and internal energies are correctly addressed [2]. The DSMC method requires as physical input data the cross sections for the elementary processes rather than the rates. To this end we have developed a code for calculating vibrational excitation-deexcitation and dissociation cross sections for atom-diatom collision processes, described in detail in [3]. It is based on the quasiclassical method for molecular dynamics, with some variants. The results for N+N2 collision process from every possible rovibrational state of the diatom have been compared with some global experimental and theoretical results, obtaining good agreement. Concerning dissociation cross sections, dynamical data (cross sections in particular) were not available. Some preliminary results about the kinetic scheme sketched above are presented here.

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Calculations on the reaction of carbon atoms with acetylene

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Low temperature measurements of kinetic rate constants have proved that there are some neutral-neutral reactions sufficiently fast to contribute to the chemistry of the *Interstellar Clouds* (ISC)[1]. There is experimental evidence[2] showing that the reactions of carbon atom in its ground state $C(^3P)$ with unsaturated hydrocarbon are indeed very fast, with rate constants in good agreement with the capture theory[2]. Furthermore, the reaction with acetylene in its ground state ($X\ ^1\Sigma_g^+$)

$$C_2H_2 + C \rightarrow C_3H + H$$
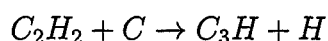
has been studied by crossed beam experiments[3], in the energy range between 9kJ/mol and 45kJ/mol. The results showed that two different reactions channels are predominant at the lowest and the highest energy investigated, attributed to the formation of two different C_3H isomers (linear and cyclic).

The key step of the reaction, the formation of the stable intermediate C_3H_2, is the subject of the present work.

We have calculated *ab initio* the interaction between $C(^3P)$ and C_2H_2 ($X\ ^1\Sigma_g^+$) as a function of two variables describing the position of the carbon atom with respect to acetylene, while all the other degrees of freedom of the system have been optimized. The quantum chemistry method that has been used is the Coupled Cluster including single and double excitations and a perturbational estimate of the triple excitations (CCSD(T)). Time dependent quantum dynamical calculations are now in progress: our aim is to determine, under reasonable assumptions, the branching ratio between the two C_3H isomers as a function of temperature.

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Near Infrared Transient Absorption Spectroscopy of Electrons in Pure Water

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In the recent past the problem of solvated electron in water and in other solvents has been the subject of many experimental and theoretical investigations [1,2]. We ourselves have performed femtosecond ($\approx$100 fs) UV pump - NIR probe transient absorption spectroscopy on the aqueous solvated electron extending the investigation at longer wavelengths and at different temperatures. Measurements have been done at temperatures from 4 to 45 C° and in the spectral range between 1.10 and 1.55 µm. In this spectral region it is possible to better disentangle the complex time evolution of the generated electrons by two photon ionization(excitation wavelength = 260 nm). Performing measurements at different temperatures it is possible to distinguish between the rate of formation of the so called wet electron and that of solvated one. From our experimental results there are evidences that the second step is dominated by relaxation processes involving changes in the local structure of water. Time constants of the process are compared to those obtained in different experiments on pure water (for example optical Kerr measurements) [3].

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State-to-state unimolecular reaction dynamics of HOCl near the dissociation threshold: the role of vibrations, rotations and IVR probed by time- and eigenstate-resolved spectroscopy.

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Abstract

We use infrared-visible double resonance overtone excitation to prepare HOCl molecules in single, well-characterized rotational levels of the $v_{OH}=6$ vibrational manifold, just above the dissociation threshold on the ground potential energy surface. Combined with time-resolved laser induced fluorescence (LIF) detection of the OH product, this approach allows us to monitor the dependence of unimolecular dissociation rate on the angular momentum (J, K_a, K_c), total energy, and vibrational character of the state of the reactant molecule as well as on number of dissociation channels available to the OH product. Dissociation rates from single eigenstates of the parent molecule are distributed over more than two orders of magnitude, in most cases with no apparent regular pattern. In several instances we observe a one-order of magnitude difference in dissociation rate between states that are nearby in quantum number and/or energy. These rate fluctuations do not appear to be directly related to either the excess energy, the total angular momentum or the vibrational character of the selected eigenstate. Superimposed on these state-to-state rate fluctuations is a general trend toward decreasing unimolecular dissociation rate with increasing K_a quantum number. The rates, which range from 1 to 300 μs^{-1}, are much slower than the 2×10^{11} s^{-1} predicted by statistical theories (RRKM, SACM). Based on our spectroscopic investigation of HOCl and on recent theoretical studies, we propose a simple model Hamiltonian to explain why the observed dissociation rates should not be expected to agree with statistical theories. The same Hamiltonian also accounts for the rate fluctuations and inverse K dependence of the average rate. Ultimately, we show that the three phenomena (slow rates, fluctuations, inverse K dependence) are all related to the slow intramolecular vibrational energy redistribution of the initially prepared state.

Conformation, dynamics and energetics of adducts of rare gases with fluorinated hydrocarbons

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Rotationally resolved spectroscopy combined with supersonic expansions[1] has allowed to obtain detailed information on the structure, dynamics and energetics of Van der Waals adducts.[2] This kind of data is available mainly for complexes of Rare Gases with very light molecules or with cyclic molecules, while little is reported for adducts with not cyclic hydrocarbons.

Here we report the results of a free jet millimeter wave absorption spectroscopy[3] investigation of difluoroethane-Ar, difluoroethylene-Ar, and difluoroethylene-Ne. The Van der Waals motions generate an enormous distortion from the rigid rotor and occasionally doublings of the rotational lines, used to obtain the above mentioned information.

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Reaction and inelastic processes in the collision
$$O_2(v >> 0) + O_2(v = 0)$$
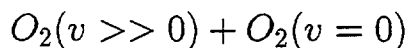
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Abstract

A reduced dimensionality model is used to study the reaction

$$O_2(X^3\Sigma_g^-, v >> 0) + O_2(^3\Sigma_g^-, v' = 0) \rightarrow O_3(X^1A_1) + O(^3P)$$
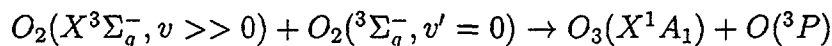
by means of time–dependent and time–independent quantum–mechanical methods. State–selected probabilities and rate constants are obtained for the reactive process as well as for the inelastic collision in which the vibrationally excited oxygen loses one or more quanta. It is found that the experimentally observed jump in depletion rates above a critical value of v could be partially explained by the vibrational relaxation rather than reaction. Reaction only becomes important for relatively high translational energies and therefore the calculated rates are too small at the temperatures of interest. It is concluded, however, that the reaction saddle point region in the potential energy surface plays a crucial role in the enhancement of vibrational relaxation.

Time-Resolved Infrared Frequency-Modulation Probing of Product Formation in the $C_2H_5 + O_2$ Reaction

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The technique of laser photolysis/cw infrared frequency modulation has been applied to the reaction of ethyl radicals with molecular oxygen. The reaction proceeds via an excited ethylperoxy radical adduct, and collisional stabilization competes with metathesis to form ethene and HO_2. Ethyl radicals are formed by the reaction of Cl atoms with ethane, initiated via pulsed laser photolysis of Cl_2, and the progress of the reaction is monitored in time through cw infrared frequency-modulation spectroscopy of the HO_2 product. Comparison with the $Cl_2/CH_3OH/O_2$ system provides measurements of the HO_2 yield, which allows the contributions of addition and metathesis to the total rate to be determined. An upper limit of 3% can be placed on OH formation from the reaction at 523 K. At low temperatures stabilization to $C_2H_5O_2$ dominates, but at elevated temperatures (> 575 K) the ethylperoxy radical is thermally unstable and a reversible addition reaction competes with production of ethene and HO_2. Biexponential time behavior of the HO_2 production allows separation of prompt, "direct" HO_2 formation from HO_2 produced after thermal redissociation of an initial ethylperoxy adduct. The prompt HO_2 yield exhibits a smooth increase with increasing temperature, with an effective activation energy of approximately 1.5 kcal mol^{-1}. The total yield at 75 Torr, which includes contributions from the redissociation of ethylperoxy radicals, rises sharply from ~10% to 100% between 575 and 675 K. Because of the separation of timescales in the HO_2 production this rapid rise can unambiguously be assigned to ethylperoxy dissociation.

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Reaction-volume applications

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Recently a new method for treating N atom chemical reactions with $N > 3$ has been developed: the reaction volume approach [1], which is based on the observation that every N atom reaction can be considered a three (or more rarely a four) center reaction, where a bond is broken while a new one is simultaneously formed: the remaining $N - 3$ (or $N - 4$) atoms play the role of spectators for the reaction. For this reason the dynamics of the atoms forming the reactive center is treated in an accurate way, *i.e.* quantum mechanically, while the other degrees of freedom can be treated approximately. One way of doing this is to choose the three hyperspherical variables [2] for the exact quantum mechanical treatment of the three centers and to project these variables out of the Hamiltonian. In this sense from the analogy with the one dimensional reaction path this method can be called a three dimensional reaction volume approach. Once these degrees of freedom have been separated out, together with the center of mass position, we are left with $3N - 6$ degrees of freedom, $3N - 9$ of which are treated within normal mode approximation in such a way that normal mode coordinates describe the displacements from a reference position and the remaining ones are three Euler angles describing the overall rotation of the system, which can be treated either classically or quantally. Such a treatment, *i.e.* the projection of hyperspherical variables, permits to use time dependent self consistent field or quantum classical methods [3], which are based on the separation into groups of the degrees of freedom, which are strongly coupled within each group, while coupling among different groups is weak. Additionally hyperspherical coordinates are the natural choice for the treatment of the three reactive centers, allowing a "democratic" handling of the reactive channels and enabling to exploit the coupled 3D wave packet approach developed for three atom reactions [4]. For the description of the motion of the atoms we need to define some reference vectors characterizing the N atom positions in a body-fixed frame, around which the particles are allowed to perform small amplitude motions. The motion of the reference vectors, as changes in hyperspherical variables take place, has to reflect any kind of arbitrary motion of the spectator atoms, as, for instance, concerted or umbrella motions. However the numerical determination of a realistic reference configuration has turned out to be a difficult task. A picture where the positions of the spectator atoms are frozen at the equilibrium geometry, though allowed to vibrate harmonically around their reference position, is easy to realize, but does not take into account the physical evolution of the system. Here we propose a recipe for the realization of the reference configuration which ensures it corresponds to a realistic picture, considering that the displacements of the atoms around the so-built reference path are treated according to a small amplitude motion approximation. The method consists of a minimization of the absolute value of the gradient, prior a minimization of the potential energy, subject to the reaction volume constraints. This model has been applied to the $H_2 + CN \rightarrow HCN + H$ reaction.

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Dynamics of atomic carbon reactions at very low kinetic energies

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In these experiments, a pulsed supersonic beam of $C(^3P_J)$ atoms is collided with a rotatable, pulsed supersonic beam of O_2, C_2H_4 or NO molecules, at beam intersection angles decremented from $\pi/2$ down to $\pi/8$. Scanning of the relative translational energy is achieved over a wide range of energies and down to values that had never been reached before. State-to-state or total reaction cross sections are derived from detection of respective CO, H and CN reaction products by laser-induced fluorescence (LIF).

$C(^3P_J) + O_2(X^3\Sigma_g^-) \to CO(X^1\Sigma^+) + O(^3P_J, {}^1D_2)$. High vibrational levels of CO product: $v = 15 - 17$ are readily detected by LIF using the $CO(A^1\Pi \leftarrow X^1\Sigma^+)$ $\Delta v = -9$ transitions around 230 nm. A clear cut-off in vibrational distribution appears between $v = 16$ and $v = 17$. State-to-state cross sections for the production of $CO(X^1\Sigma^+, v = 15 - 16)$ increase monotonically when decreasing kinetic energy from 90 to 4.4 meV, as expected for an exoergic process without an energy barrier. The cross section for $CO(X^1\Sigma^+, v = 17)$ exhibits an energy threshold at ca. 45 meV which is consistent with the excitation limit of the reaction path leading to $CO(X^1\Sigma^+) + O(^1D_2)$ [1].

$C(^3P_J) + C_2H_4(X^1A_g) \to C_3H_3(X^2B_2) + H(^2S_{1/2})$. H product is detected by LIF on the $L\alpha$ transition at 121.6 nm. The total reaction cross section increases when decreasing kinetic energy between 100 and 4.4 meV, with no sign of an energy threshold. A functionality $(\epsilon_{tr})^{-0.56}$ is found, which results in a rate coefficient temperature dependence $k(T) \propto (T)^{-0.06}$, in fair agreement with experimental kinetic data $(k(T) \propto (T)^{-0.13})$, recently obtained at temperatures from 295 K down to 27 K [2].

$C(^3P_J) + NO(X^2\Pi_r) \to CN(X^2\Sigma^+) + O(^3P_J)$. CN radicals are probed by LIF on the $(B^2\Sigma^+ \leftarrow X^2\Sigma^+)$ $\Delta v = -2$ sequence around 460 nm. State-to-state cross sections for production of $CN(X^2\Sigma^+, v = 2 - 4)$ increase from 94 to 4 meV with no sign of an energy threshold. CN product vibrational excitation remains fairly constant in this energy range but rotational excitation tends to decrease significantly.

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An Experimental Study of Collisional Rotational and Electronic Energy Transfer between CN($A^2\Pi$) and Ar: Λ-doublet Propensities and Gateway Effects

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Optical-optical double resonance has been employed to investigate rotationally and electronically inelastic transitions from specific, highly rotationally excited Λ-doublet, fine-structure levels of the CN($A^2\Pi$) electronic state, induced by collisions with argon. High rotational levels of the CN($X^2\Sigma^+$) radical were prepared by 193 nm photolysis of BrCN diluted in slowly flowing Ar at total pressures of 0.5 – 1 Torr. After a suitable delay, specific fine-structure Λ-doublet levels of CN($A^2\Pi$, v = 3, $N \approx 60$) were prepared by excitation with a pulsed dye laser on various rotational lines in the $A^2\Pi - X^2\Sigma^+$ (3,0) band. Collisionally populated levels were probed after a short delay by laser fluorescence excitation in the $B^2\Sigma^+ - A^2\Pi$ (3,3) and $B^2\Sigma^+ - X^2\Sigma^+$ (3,7) bands. Absolute state-to-state rate constants were determined by comparison of the fluorescence signals for detection of the initial and final levels, and absolute total removal rate constants were obtained by following the decrease in the signal for detection of the initial level *vs.* the pump-probe delay.

Dramatically different final rotational state distributions were observed for collision-induced rotational transitions from initial Λ-doublet levels of A' and A'' symmetry, independent of the fine-structure label F_i. These propensities are believed to arise from approach in a "helicopter" orientation on the more attractive Ar–CN(A) A' potential energy surface, followed by curve crossing to the A'' potential energy surface correlating with the next lower rotational asymptote. The measured state-to-state rate constants compare very well with theoretical rate constants calculated by Millard Alexander (University of Maryland) in a quantum mechanical collisional treatment using *ab initio* CN–Ar potential energy surfaces computed by A. Berning and H.-J. Werner (Universität Stuttgart)..

A crossing of the $A^2\Pi$ v = 3 $F_1 f$ rotational/fine-structure manifold with the $X^2\Sigma^+$ v = 7 f manifold occurs at $N = 62$. We have investigated the importance of this "gateway" in facilitating collision-induced electronic transitions between these manifolds. The total removal rate constant for the perturbed $N = 62$ level is substantially larger than for those of neighboring unperturbed levels, indicative of the magnitude of the perturbation-assisted $A \rightarrow X$ rate constants. Moreover, the final-state distribution is strongly dependent on the identity of the initial state.

Non adiabatic effects in the photodissociation of SiO

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This study concerns the photodissociation of SiO by absorption from the first vibronic state of the ground electronic surface $X^1\Sigma^+$. In this photodissociation process, the contributing states must have a large transition moment with the ground state. Thus the most likely candidate is the $E^1\Sigma^+$ state. The non adiabatic interaction between E and the upper $F^1\Sigma^+$ state near R=4.5 bohr (cf Figure) should lead to perturbations in the photodissociation cross section for energies ranging in the region of the avoided crossing.

All the relevant ab initio electronic potentials and transition moments involved in the X-E and X-F transitions as well as the E-F non adiabatic radial coupling matrix element have been calculated at the MCSCF-CI level, using the MOLPRO[1] package. Then two different approaches (time-independent and time-dependent methods) have been used to obtain the photodissociation cross section.
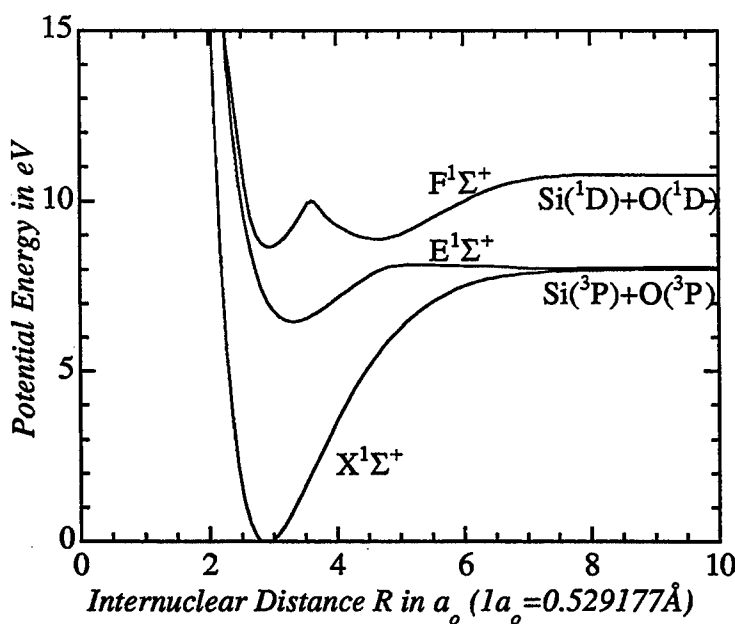
Figure 1. SiO Potential Energy versus Internuclear Distance R.

[1] MOLPRO is a package of ab initio programs written by H.-J. Werner, P. J. Knowles, with contributions by J. Almlöf, R. D. Amos, M. J. O. Deegan, S. T. Elbert, C. Hampel, W. Meyer, K. A. Peterson, R. M. Pitzer, A. J. Stone and P. R. Taylor.

STATE-TO-STATE THREE-ATOM REACTIVE SCATTERING USING ADIABATIC ROTATION APROXIMATIONS

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There has been a great progress in doing exact quantum dynamics calculations of atom-diatom reactions, using both time-independent and time-dependent methods . However, an exact treatment of rotation presents a problem that scales in effort as J^2 for wavepackets methods and as J^3 for coupled-channel methods, due to the coupling among the K-states, where K is the projection quantum number of the angular momentum J on a body-fixed axis. This means that approximate dynamical methods for $J>0$ will always play an important role in extending the capability of theory to more complex problems.

In this work we explore the applicability and extension of the so called Rotationally Adiabatic Approximation [1] to state-to-state reactive scattering calculations. The Rotationally Adiabatic Hamiltonian is given by

$$\hat{H} = \hat{H}_{J=0} + E^{JK}_{A,B,C}(r,R,\gamma) \tag{1}$$

where $E^{JK}_{A,B,C}(r,R,\gamma)$ is the rotational energy of a prolate symmetric top rotator. The rotation constants, A, B, and C are functions of the nuclear configuration. $E^{JK}_{A,B,C}(r,R,\gamma)$ is thus a centrifugal potential that includes centrifugal distortion (because the rotation constants vary with internal geometry) but neglects Coriolis coupling.

Using adiabatically adjusting principal axis of inertia hyperspherical (APH) coordinates (ρ,θ,χ) [2] the total hamiltonian $\hat{H}$ can be expressed as $\hat{H} = \hat{H}_{J=0} + \hat{H}_{J>0}$ where $\hat{H}_{J>0} = A(\rho,\theta)J_x^2 + B(\rho,\theta)J_y^2 + C(\rho,\theta)J_z^2 + T_c$. This total hamiltonian $\hat{H}$ can be reduced to a Rotationally Adiabatic Hamiltonian, eq. (1), by neglecting the Coriolis term T_c and diagonalizing $\hat{H}_{J>0}$ in a basis of parity adapted combinations of Wigner $D^J_{MK}(\alpha,\beta,\gamma)$ functions. In this case $E^{JK}_{A,B,C}(\rho,\theta)$ are the energy levels of an fluid rotor. In this way we have included asymmetric coupling terms that couple K-states of the same parity.

Results using both types of Rotationally Adiabatic Approximations [3] in comparison with exact and approximate calculations will be presented for a series prototypic reactions: $H + D_2, D + H_2, F + H_2, Cl + H_2$ and $Li + HF$.

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VELOCITY MAP IMAGING AS A POWERFUL TOOL TO STUDY COLLISIONAL AUTOIONIZATION PROCESSES

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The collision of an excited atom, A^*, with a target molecule, BC, characterized by an ionization potential lower than the atom excitation energy, leads to autoionization of the intermediate $[A^*...BC]$ complex. The product of autoionization, the ionic complex $[A...BC^+]$, will subsequently evolve along different ion product channels: Apart from the formation of BC^+ ions in different vibronic states (Penning ionization) and associate ions ABC^+ (associative ionization), an ion-molecule reaction between ground state A and BC^+ may occur (rearrangement ionization) as well as the dissociation of sufficiently excited BC^+ molecular ions (dissociative ionization) [1,2].

Such processes have been studied hitherto by measuring the corresponding total and partial ionization cross sections through mass spectrometric detection of product ions [1,2] or by analyzing the energy distribution of the product electrons at different collision energies of the neutral reactants [1,2]. An additional, very powerful technique is the measurement of the angular and energy distribution of product ions in crossed beam experiments [2,3]. The corresponding results provide some very detailed information with regard to the dynamics of the reaction. However this technique, which has been introduced for collisional autoionization processes about 25 years ago [4] has been applied to only few systems because of the many experimental difficulties and the long integration time necessary to obtain statistically reliable results.

The ion-imaging technique has been introduced and developed in the last decade by D.W.Chandler [5] and P.L.Houston [6] and, very briefly, consists in mapping the spatial distribution of charged particles onto a two-dimensional (2-D) detector. From the 2-D image the full 3-D information can be reconstructed by means of an Abel inversion method. Recently, a significantly improved imaging technique, velocity map imaging, was reported by A.T.J.B Eppink and D.H. Parker [7] which allows for a much better spatial resolution.

Velocity map imaging which provides both full angular and kinetic energy information is used so far mainly for photo-dissociation processes. For the first time, it has been applied in this laboratory for collisional autoionization in thermal energy collisions of metastable neon atoms with Ar and Kr. The respective results appear to be very promising with the time needed for accumulating a statistically meaningful result being very short (in the order of a few minutes) and the resolution being sufficiently high. A peak of product ions centered along the direction of the ground state atoms Ar and Kr, respectively (forward peak) could be observed, indicating a Penning ionization process occurring essentially at large impact parameters. A second ion peak appearing along the center-of-mass direction should be attributed to the formation of associate ions, namely $NeAr^+$ and $NeKr^+$, respectively as it is expected from simple dynamical considerations [3,4]. On the basis of total and partial cross section measurements [8] the associate ion peak is assumed to rapidly decrease with increasing collision energy.

The obtained results already show that velocity map imaging is a promising means in studying the dynamics of collisional autoionization processes. Nevertheless, some experimental improvements are still to be achieved. In particular, secondary ionization of neutrals induced by photons which arise from the electrical discharge represents a drawback. As a consequence, the Penning ion peak (forward) might be partially overlapped by this secondary ion signal preventing by now an absolute determination of the branching ratio of the product ions . This problem should, however, be fully overcome using an appropriate chopping device in order to discriminate the discharge photons against the product ions. We are presently working in such a direction.

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BANDSTRENGTH ANALYSIS OF $\Delta v = 0, \pm 1$ VIBRATIONAL SEQUENCES OF THE NF (b $^1\Sigma^+ \to$ X $^3\Sigma^-$) EMISSION. ESTIMATE OF THE GROUND STATE DISSOCIATION LIMIT.

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The $\Delta v = 0$ and ± 1 sequences of the NF (b $^1\Sigma^+ \to$ X $^3\Sigma^-$) spin forbidden emission are produced in a flowing afterglow apparatus by NF_3 windowless photolysis [1], and the emission strengths analized.

Vibrational populations are shown to be in a statistical equilibrium. It is seen, however, that the emission intensity of a small interval of bands falls below the exponential (Boltzmann) distribution. This behaviour is not expected, and is attributed to interactions between the b $^1\Sigma^+$ emitting state with the continuum corresponding to ground state dissociation (Fig 1). A value of 68.9 kcal/mol for the NF X $^3\Sigma^-$ dissociation limit is thus estimated.
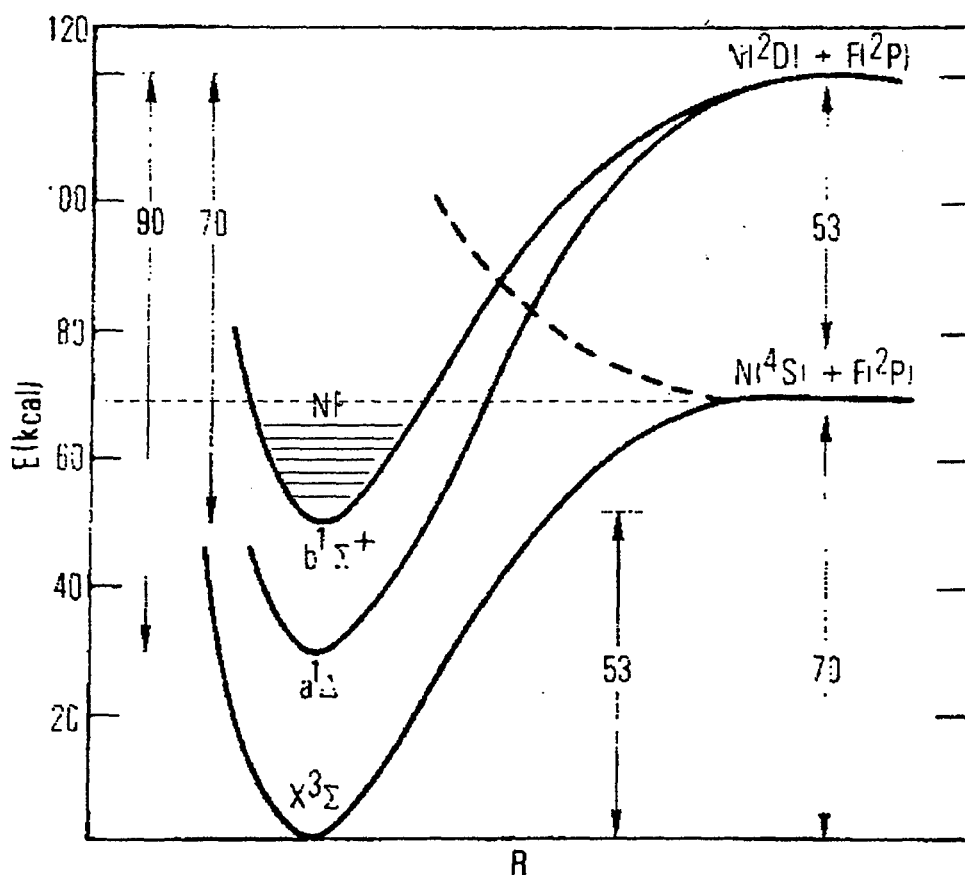
Fig. 1. Potential energy diagrams of NF.

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Inelastic Collisions of Oriented NO Molecules with Ar

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A beam of NO molecules is state selected in the upper Λ-doublet component of the J=1/2 rotational level of the X $^2\Pi_{1/2}$ ground state using an electric hexapole focuser. After state-selection, the NO molecules can be oriented in a homogeneous electric field. In combination with a crossed beam geometry this enables us to study orientation effects along with the role of parity breaking on collision-induced rotational excitation of NO.

In an electric field rotational states can no longer carry a well-defined parity. This parity breaking is demonstrated by recording the Laser Induced Fluorescence (LIF) spectrum of the $\gamma(0,0)$ band at 226 nm. Due to the mixing of the Λ-doublet components transitions from the selected Λ-doublet component that are parity forbidden at zero electric field become allowed in an electric field. A quantitative analysis of the LIF intensity ratio for the zero field forbidden and allowed transitions (provided that saturation remains absent for all transitions) shows that the observed degree of parity breaking is proportional to the degree of orientation. This is a necessary prerequisite for quantitative exploration of steric effects in inelastic collisions.

The rotational inelastic scattering of oriented NO with Argon atoms has been studied in the crossed beam setup. The steric asymmetry (defined as the difference between the inelastic collision cross section with the N-end in front and the one with the O-end in front divided by the inelastic collision cross section with randomly oriented incoming NO molecules) was determined as function of the final rotational product state. As most striking result it was found that the steric asymmetry changes sign with $\Delta J=1$ for the final product state. The agreement between the experimental results and theoretical calculations regarding the sign and strength of the steric asymmetry, as well as its insensitivity for parity conserving/breaking final rotational states is remarkable. Further experimental and theoretical work is in progress to elucidate these steric phenomena.

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"Combined quantum/classical description of coherent vibrational dynamics in diatomic molecules interacting with a gas environment."

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A novel precise mixed quantum-classical algorithm for the treatment of the vibrational quantum state evolution for diatomics interacting with dense inert gases is developed [1]. In the present approach, the vibrational coordinate is treated quantum-mechanically. The molecular rotation, as well as the center–of–mass motion and the gas dynamics are treated classically. Within the present approach the classical equations for the rotational motion have no singularities. A symplectic algorithm is used for the propagation assuring a good conservation of the total energy. The method is applied to interprete data obtained from femtosecond pump–probe experiments. In particular, the decay of the pump–probe signal via the thermal average over rotational states and by collisions with the buffer gas is considered. Numerical results are in good correspondence with available experimental data on I_2 in rare gas surroundings. The developed approach can be applied to a wide scope of problems related to studies of molecules embedded in gases or liquids, being adsorbed on the surface of solids as well as in more complicated hosts like zeolites and nanotubes.

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Study of the internal energy redistribution in molecules
by following the time evolution of laser-induced thermal gratings

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Laser-induced gratings are spatial modulations of the complex refractive index of a medium produced by the interference of two laser beams as a result of resonant or non-resonant light-matter interactions [1]. The period of the modulation is equal to the interference fringe spacing, determined by the excitation wavelength λ_P and the angle of beams intersection. In the gas phase at resonant excitation of gratings the population of atomic/molecular energy levels involved is changed by selective laser energy deposition through dipole- or Raman-active transitions. Subsequent release of internal energy in the form of heat due to collisional relaxation may lead to the formation of thermal gratings (LITGs). Laser-induced gratings are detected by scattering of a probe laser beam of another wavelength, λ_R, directed at a Bragg angle to the planes of the fringes. By using a cw laser for probing a LITG excited by a pulsed source, its temporal evolution can be studied. The latter can be quantitatively described using the linearised hydrodynamic equations and rate equations of collisional redistribution of internal energy. A solution is a superposition of a standing acoustic wave, created by adiabatic compression, and a stationary density modulation, due to isobaric heating. The acoustic wave in a gas is damped by viscosity and heat conduction, while the stationary density modulation decays by heat conduction alone. The temporal behavior of LITGs depends on the rate of the energy thermalisation: fast energy release generates a standing acoustic wave and a stationary density modulation with equal amplitudes; slow energy release favours the formation of the stationary density modulation whereas the development of the acoustic contribution is supressed. In case of a multi-step thermalisation process, with different time constants involved, oscillatory and stationary contributions to LITGs can be observed.

The possibilities of the LITG technique in investigations of molecular relaxation processes are demonstrated for NO_2 excited via vibronic transitions of the $^2B_1 \leftarrow {}^2A_1$ band at λ_P = 466-490 nm [2], the gratings being probed by cw radiation at λ_R = 515 nm. Mixtures of 0.4 mbar of NO_2 with Ar, N_2 and CO_2 at temperatures T = 298-450 K and buffer gas pressures up to 5 bar were employed. Buffer gas slows down mass and thermal diffusion in the medium and stimulates electronic quenching, v-v' and vR-T relaxation of excited NO_2 molecules, that results in a significant enhancement of the LITG signal. The spectral linewidth of the pump laser and collisional line broadening provided rotationally non-selective excitation of molecules into an upper vibronic state. The gas temperature was measured from the period of acoustic oscillations in LITGs signals using the dependence of sound velocity on temperature. The temporal behavior of the scattering efficiency in different mixtures depicts manifestations of different fast and slow processes of release of absorbed laser energy.

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Photoinitiated harpooning reaction in the Ba...FCH3 complex: femtosecond dynamics and product state analysis

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An intracluster harpooning reaction is investigated on the femtosecond timescale for the first time in a metal atom-halide compound. In the experiment weakly bound Ba...FCH3 complexes are formed in a molecular beam by adiabatic expansion of a gas mixture containing laser desorbed Ba vapor and CH_3F molecular gas (10%) in He (1 bar) carrier gas. Via resonant excitation of the complexes by fs laser pulses of the wavelength 618nm the bimolecular reaction $(Ba...FCH_3)^* \rightarrow BaF + CH_3$ is initiated, the latter being characterized by a valence electron transfer from the excited Ba atom to the F atom in CH_3F according to the harpooning mechanism.

In pump-probe measurements with 130fs laser pulses at probe wavelengths of 267nm and 400nm, respectively, the ions are detected in a TOF-mass spectrometer. By monitoring directly the decay of the parent complex and the corresponding formation of the BaF reaction product a reaction time of (270 ± 30)fs is found.

The determination of the kinetic energies of the fragments BaF and CH_3 by analysis of the BaF^+ mass peak broadening leads to an estimation of the reaction's energy balance. Thus, the vibronic energy of the BaF product is obtained.

The experimental results are compared with our *ab initio*-calculations including the relevant potential energy surfaces.

Ultrafast photodissociation dynamics and quantum beats in CS_2 excited by femtosecond laser pulses at 194...207nm

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Tunable deep UV femtosecond pump-probe ionization spectroscopy at wavelengths between 194nm and 207nm has been applied to investigate the energy-dependent predissociation for the main vibronic levels in the $^1B_2$ state of CS_2.

The transition from the $^1\Sigma_g^+$ electronic ground state to the predissociative $^1B_2$ ($^1\Sigma_u^+$) state has been the subject of numerous investigations in the past. However, the different indirect methods to estimate the lifetimes of the $^1B_2$ state's vibrational bands are very uncertain and sometimes contradictory.

Using the fourth and third harmonic of a tunable commercial Ti:sapphire-fs-laser and amplifier system to excite and ionize the CS_2 molecules in an adiabatically cooled molecular beam along with ion detection in a TOF-mass spectrometer the dependence of the $^1B_2$ state's lifetime on the excitation energy was studied yielding a decrease from 620fs down to 180fs for an increase of the energy from 6.0eV to 6.4eV. A discontinuity at about 6.2eV is due to the influence of a well-known energetic barrier for a change from a completely bent to a quasilinear excited state geometry at higher energies.

Furthermore we observed a reproducible coherent modulation of the signals for such excitation wavelengths where more than one vibrational band is excited simultaneously in the $^1B_2$ state of CS_2. The oscillation time period agrees with the energy difference of the respective absorption lines covered by the spectral width of the ultrashort laser pulses. Hence, despite the fast predissociation we were able to monitor quantum beats arising from simultaneously excited vibrational bands demonstrating the coherent nature of the excitation process.

Electronic energy transfer in I_2 (E) + He, Ar, I_2 (X) collisions

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Using two-color photoexcitation, we have prepared single rotational levels in v = 0 of the E ion pair state of I_2 and have explored the collision-induced energy transfer processes that occur with He, Ar and I_2 (X) under single collision conditions. In I_2 (E) + I_2 (X) collisions we observe efficient electronic relaxation of I_2 (E); the D electronic state is selectively populated with a cross section of ≈ 20 Å^2. Single collisions of I_2 (E) with Ar or He produce I_2 in the D electronic state, but also populate the β electronic state; these processes occur with cross sections of < 3 Å^2. For all electronic relaxation pathways, the vibrational distributions are consistent with a hybrid propensity law that incorporates both Franck-Condon and energy scaling components. To date, we have prepared three different I_2 initial rotational states (J = 23, 55 and 98); the cross sections for electronic relaxation are insensitive to the initial rotational state.

Trajectory calculation of velocity dependent energy transfer transition probabilities, P(E',E,v), for the system H₂O (E$_v$, T$_{rot}$) + Ar

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Determination of rate coefficients of chemical reactions requires a solution of a master equation

$$\frac{d[(A(E,t)]}{dt} = -\int_0^\infty \int_0^\infty \omega(v) P(E,E',v) [A(E',t)] dE' f(v) dv +$$

$$\int_0^\infty \int_0^\infty \omega(v) P(E,E',v) [A(E',t)] dE' f(v) dv - k(E)[A(E,t)] \qquad (1)$$

where $k(E)$ is the RRKM rate coefficient, *[A(E,t)]* is the concentration of *A* at energy *E* and time *t* and $\omega(v)$ and *P(E',E,v)* are the velocity-dependent collisional frequency and energy transfer probability function.

The dependence of $\omega(v)$ and *P(E',E,v)* on v is not known. Therefore they are assumed constant independent of v, which, in the case of *P(E',E,v)* is clearly a gross assumption which can lead to erroneous results.

In principle, *P(E',E,v)* can be obtained from trajectory calculations. In this report, *P(E',E,v)* for the relaxation of vibrationally excited H₂O in collisions with Ar is calculated directly from trajectory computations at a given initial v. The initial vibrational energy is 26250 cm^{-1} and the rotational temperature is 1000K. For each initial condition 5000 trajectories were run, and the average energy transferred in deactivating collisions, $<\Delta E>_d$ and the cumulative transition probabilities, *Q(ΔE)* were calculated as a function of v. Then, *P(E',E,v) = d[Q(ΔE)]/d(ΔE)* was obtained at each velocity.

Two main results were obtained:
1) $<\Delta E>_d$ is linearly dependent on v.
2) *P(E',E,v)* can be represented by a three exponential function for downward collisions, and by a double exponential function for up transitions. Both of them are function only of the average energy transferred in deactivating collisions,$< \Delta E>_d$. Thus for the down wing

$$P_d(E',E,v) = \left(\frac{A}{a < \Delta E >_d}\right) exp[(-E'-E)/a < \Delta E >_d] +$$

$$\left(\frac{B}{b < \Delta E >_d}\right) exp[(-E'-E)/b < \Delta E >_d] + \left(\frac{C}{c < \Delta E >_d}\right) exp[(-E'-E)/c < \Delta E >_d] \qquad (2)$$

where *A ,a, B, b, C* and *c* are velocity independent constants.

Therefore, *P(E',E,v)* can be written directly as a single function of v to be used in eq(1).

Quantum dynamics at a conical intersection: some general rules emerging from a model study

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We report some results of our study of the quantum dynamics in a two-state, two-mode conical intersection. The numerical investigations concern the role played by the variation of the oscillator frequencies in the diabatic transition probability, the influence of the initial conditions and of the geometrical setup of the two potential energy surfaces involved. These results show regularities that can be summarized in a few general rules which may help in interpreting time-resolved observables, like those coming from femtosecond pump and probe experiments. It is shown, in particular, that the geometrical disposition of the crossing surfaces has a deep influence on the features of the time-resolved fluorescence spectrum, which can either be monotonically decreasing or exhibit marked oscillations. These rules can be used also as a qualitative guide in interpreting fluorescence spectra in large molecules.

Non adiabatic coupling and radiationless transitions in molecules with charge transfer excitations between weakly-coupled aromatic rings (biarils and related molecules)

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Aromatic systems built by weakly interacting sub-units (like bi-phenil, for example) are interesting subjects for studying energy and charge transfer processes. Here we develop a general interpretative scheme for the electronic relaxation of systems in which the first excited singlet involve charge transfer between such sub-units. On the basis of simple quantum models we show that the torsional motion of one of the moieties with respect to the other is deeply involved in the radiationless decay of such excited states, due to the non adiabatic coupling between the two electronic states. The efficiency of the non radiative decay, however, is very sensitive to the ability of the torsional motion to dissipate its excess energy towards solvent modes and/or to a more or less dense manifold of intra-molecular modes. To study these processes we couple the quantum calculations to a stochastic approach based on a Fokker-Plank equation for the distribution function in the coordinate space.

μSR Kinetics Studies of Unimolecular Dissociation: termolecular rate constants for Mu +NO, O_2 and CO .

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The positive muon (μ^+) is produced 100% spin polarized and forms the Muonium atom (Mu$= \mu^+ e^-$), an isotopic cousin of the H-atom, *but* with 1/9'th the mass. As such the study of muonium reactivity provides for the measurement of *remarkable* Kinetic Isotope Effects (KIEs). In the present studies, Mu undergoes both chemical addition and spin exchange reactions, and this affects the hyperfine interaction between muon and electron spins, causing depolarization of the muon. These processes have been measured in μSR experiments for the reactions of Mu with NO, CO and O_2, over wide ranges of pressure and for different moderators (He, N_2, Ar and CH_4) at room temperature, up to 500 bar in the cases of NO and CO, and over a range of temperatures as well in the cases of O_2 and CO. The kinetics are dominated by termolecular addition (rate constants k_0)over the pressures studied for both NO and O_2 and both reveal *inverse* KIEs, with $k_{Mu}/k_H \sim 1/5$, indicative of enhanced unimolecular dissociation of the Mu isotopic analog. For the Mu+CO reaction, the kinetics appear to be much more complex, with a clear quadratic pressure dependence which becomes more and more enhanced at lower and lower temperatures. This may inidicate the importance of specific resonance states in the MuCO* adduct formed and/or may be a more general phenomenon for H-atom addition reactions for small molecule systems at high enough densities. From the linear portion of this dependence we find that k_0 for the Mu+CO reaction is about a factor of 50 *slower* than for either NO or O_2, presumably partly the result of a non-zero electronic barrier. The question of resonance states in MuCO* (and MuO_2^*) is an interesting one in the light of current interest in such levels in the H-atom analogs, since the density of states for the Mu species is much less. The inverse KIEs for the O_2 and NO reactions have been analyzed with the theoretical approach of Troe, which qualitatively reproduces the results, but the effects of quantum tunneling have not been included.

Femtosecond transient absorption spectroscopy with chirped continuum probing: coherence effects in Azulene S_1 electronic state.

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The dynamics of the S_1 state of Azulene has been the subject of many theoretical and experimental papers.In liquid solution and at room temperature the S_1 state is almost non-fluorescent and population lifetime has been determined to be of the order of 1-1.5 ps depending on the solvent.

We have undertaken a study of the S_1 state by means of UV-Vis transient absorption (TA) spectroscopy with the aim of better characterize the dynamics of this state. TA spectroscopy with continuum probing provides both spectral and dynamical information concerning electronic excited states. In the present case it has been possible to record the transient spectrum from the S_1 state and its temporal evolution. In the spectral region investigated (350-650 nm) the spectrum shows a broad structure with peaks at 380 nm and 440 nm and, additionally, shoulders at 366 nm, 405 nm and 480 nm. The intensity of the bands, except for the shoulder at 366 nm, decreases with an exponential law with time constant of 1.2 ps in cyclohexane and 1.4 ps in acetonitrile. These values are in good agreement with those previously reported for the lifetime of the S_1 state. At times between 200 and 700 fs from the excitation it is possible to clearly observe an interference feature that moves to lower frequencies with increasing delays. Such phenomenon is due to the dispersion of the continuum due to the crossing of the entrance window of the flowing cell and it would not be observable if the probe was unchirped. We interpreted the appearance of this interference feature as due to the interaction between a population contribution (two step process) and a coherent one (two photon process) observable because of the particular distribution of the electronic levels in azulene.
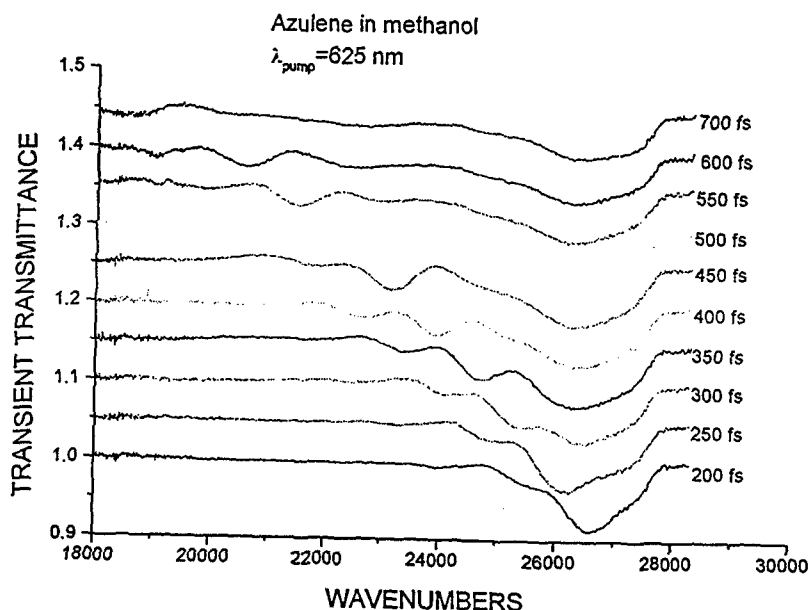
Azulene in methanol
$\lambda_{pump}=625$ nm

Photodissociation of an alkyl nitrite at a liquid surface:

Flight time distributions of NO and HNO

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Abstract

The photochemistry at a gas-liquid interface was investigated by time-of-flight / quadrupole mass spectroscopy. A liquid film of dodecyl dinitrite ($ONO(CH_2)_{12}ONO$), dissolved in squalane ($C_{30}H_{62}$), was excited to the S_1 and S_2 states by irradiation at 355 nm and 275 nm, respectively. At both wavelengths NO and HNO were the only photoproducts ejected into the gas phase under the low laser fluence which precludes thermal effects. A ratio NO/HNO of 2-4 was found.

Model calculations which take into account laser photolysis of the chromophore, diffusion and thermal surface evaporation of NO and HNO, and the condensed-phase kinetics of radical reactions, can account for the major (slow) component of the NO signal, and the entire HNO signal. Ejection of a minor fraction (4%) of hyperthermal NO was also observed. The fast NO fragments are characterized by translational temperatures in the range 500-2000 K. The results are compared with photodissociation studies of alkyl nitrite monomers, clusters and monolayers on solid surfaces.

Photodissociation of carbonyl cyanide CO(CN)$_2$: From single molecules to clusters and cryogenic matrices

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Abstract

We present a comparative study of the photodissociation of carbonyl cyanide CO(CN)$_2$ photolyzed at 193 nm, as it occurs (a) in isolated gas-phase molecules, (b) in jet-cooled clusters [CO(CN)$_2$]$_n$ and [CO(CN)$_2$]$_m$Ar$_n$, and (c) isolated molecules in cryogenic Ar and Xe matrices. The gas phase results were obtained using photofragment translational energy spectroscopy, while those in the matrix were monitored infrared spectroscopy.

According to a comprehensive analysis of the CO(CN)$_2$ monomer results in the gas phase, a major fraction of ≈94% of the excited molecules decay to OCCN + CN (radical channel). Besides this a molecular decay to CO+NCCN with a yield of ≈6 % was observed. The average kinetic energy of the fragment pairs was determined to be 37 and 190 kJ/mol for the radical and molecular decay channel, respectively, corresponding to 18% and 30% of the available energy. A minor fraction of the OCCN fragments (≈18 %) undergo spontaneous secondary dissociation to CO+CN.

The cluster photoproducts were also analyzed by photofragment translational spectroscopy. The fragments CO, CN, OCCN, NCCN and CO(CN)$_2$ were identified. The ratio of the products OCCN and NCCN, is larger or equal to the ratio found for isolated CO(CN)$_2$ molecules. We observed a large fraction of OCCN and NCCN fragments with very low kinetic energies. ($\langle E_T \rangle \approx$ 3-4 kJ/mol). Since these slow species possess less than 10% of the kinetic energy found for isolated molecules, they must originate from the cluster interior.

The major fragment species of gas phase monomers and clusters, CN+OCCN, were not detected in the matrix environment. This is attributed to complete caging and recombination of the nascent species in the matrix. Three new IR appear with an initial increase followed by a decrease upon prolonged irradiation. Based on the kinetic behaviour and a comparison with calculated ab initio frequencies, these IR bands are attributed to the compound CO(CN)(NC) formed by photoisomerization of the parent molecule. The final products found after prolonged irradiation are CO, NCCN and a small amount of CNCN. A reaction scheme is presented which accounts for the various photoproduct species of CO(CN)$_2$ in caged environment.

Ultrafast photodissociation dynamics of metal carbonyls

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It has long been known that metal carbonyls eliminate a CO group on photolysis in the UV. The dissociation was believed to occur via a directly repulsive potential energy curve [1] to produce the ground state of an unsaturated carbonyl which is sometimes a triplet. It has also been claimed that several CO groups can be more or less synchronously eliminated [2]. We investigated $M(CO)_6$ (M = Cr, Mo, W), $Fe(CO)_5$ and $Mn_2(CO)_{10}$ by femtosecond spectroscopy. The molecules were pumped by one photon at 267 nm and then probed by multiphoton ionization at 800 nm and mass selective detection of the resulting parent and fragment ions [3]. The different ions contain different information which supplements each other. Often we can monitor the motion of the neutral molecule all along the potential energy surfaces from the Franck-Condon region down to the product ground state.

In all cases the molecule changes the electronic state within 10-30 fs at least once, probably via conical intersections induced by Jahn-Teller splitting of the many degenerate states, before it then eliminates a single CO group within few tens of femtoseconds. The resulting unsaturated carbonyl is produced in the singlet excited state S_1. The initial geometry is nearly the original one with just one CO lacking (C_{4v} for $M(CO)_5$). From there, the molecule leaves within typically 50 fs through a Jahn-Teller induced conical intersection to S_0. This intersection is a state which is degenerate by symmetry (D_{3h} for $M(CO)_5$, T_d for $Fe(CO)_4$). The motion along this relaxation coordinate is a pseudorotation, exchanging the ligands within the molecule. Pseudorotation seems to be widespread after photodissociation of metal carbonyls, and we interpret in this way also the results of [4] on $Mn(CO)_5$ produced by photolysis of $Mn_2(CO)_{10}$ at 310 nm. An exception is $Ni(CO)_3$ (from photolysis of $Ni(CO)_4$) where the Jahn-Teller effect does not connect S_1 with S_0; therefore this molecule shows luminescence with a lifetime (15 µs) nearly 9 orders of magnitude longer than that of $M(CO)_5$! Coherent oscillation of the wavepacket along the pseudorotation coordinate has been observed in all the investigated cases, except with $Fe(CO)_4$ which has no suitable resonance. It is interesting that this motion is perpendicular to the initial acceleration (in contrast to the usual expectation for impulsive excitation).

Only after arrival at S_0 a second (and third, if the energy suffices) CO is eliminated in a thermal process (≥ 1 ps). The unsaturated Fe carbonyls have triplet ground states. Their formation by intersystem crossing takes nanoseconds.

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Rotational Energy Transfer from CN(B,v=0,N)

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State-to-state and total rotational energy transfer rate constants have been measured for helium as the collision partner for a number rotational states of CN(B,v=0) from N=0 to N=13, including both perturbed and unperturbed levels. Parent states were prepared by dye laser pumping of CN(X,v=0) produced in the photolysis of cyanogen by a pulsed molecular fluorine laser. Spectra of the resulting (B-X) fluorescence obtained for various He pressures from 100 to 800 mTorr provided the data from which state-to-state RET rate constants were obtained. Total RET rate constants were obtained by observing parent line fluorescence with the aid of a transient digitizer. A weak propensity for odd jumps in N was observed in contrast to a strong even propensity observed by Filseth and co-workers for CN(X,v=1,N). In addition, a relatively flat dependence of the total RET rate constant on N was observed, in contrast to the strong decrease with increasing N observed for CN(X,v=1,N).

Quasiclassical dynamics
of the H_2 + H_2 reaction and dissociation

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The H_2 + H_2 reaction is progressively attracting more attention from theorists not only because it is a suitable prototype for four atom reactions but also because it is of high practical interest. This system is, in fact, important for astrophysics, combustion and spacecraft modeling applications.

The first aim of the present work was to compare quasiclassical estimates of nonreactive dissociative, reactive (exchange) and reactive dissociative properties of the H_2 + H_2 reaction calculated on the PES of ref. [1] with quantal reduced dimensionality model [2] and quasiclassical full dimensional, small impact parameter [3] values reported in the literature.

Model quantum results reasonabily well agree with quasiclassical calculations performed by imposing the corresponding dynamical constraints. Therefore, differences between model quantum and 3D quasiclassical calculations can be mainly attributed to the constraints of the model. As a matter of fact, quassiclassical calculations show that the behaviour of the various processes has a different dependence upon the impact parameter. In fact, while the opacity function of reactive events drops dramatically with the impact parameter that for reactive and nonreactive dissociative events increases to a maximun before dying smoothly at higher impact parameters.

Another objective of the present work was to study the effect of varying the vibrational, rotational and translational energy on the value of the considered cross sections (nonreactive dissociative, reactive and reactive dissociative). An increase of the vibrational excitation of one the collision partners enhances all these cross sections (at the expenses of the purely non reactive and non dissociative cross sections). The effect is large for reactive dissociation and it is smaller for reactive and nonreactive dissociative cross sections. The rotational energy has an effect on reactivity smaller than that of vibrational energy. When rotational excitation is increased, all three considered cross sections increase, with reactive dissociation being the most affected. The effect of varying the translational energy of the system is almost negligible.

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R2PI spectroscopy of chiral systems

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In the past years significant progress has been made in elucidating the ground state properties of weakly bound complexes. Much of the interest in study of clusters relies on the fact that the measured properties offer new opportunities to examine the nature of molecular interaction. The intermolecular forces acting in these systems are much weaker than those of chemical bond and their characterization has been made possible by use of experimental techniques as supersonic beam coupled with resonance multiphoton ionization spectroscopy. The aggregates are usually generated by supersonic expansion through a pulsed nozzle of rare gas seeded with molecules under study. The clusters formed can be characterized by mass resolved resonant spectroscopy and information on the electronic shift, intermolecular vibrations and bond energies of cluster measured [1].

In this paper experiments on 1c and 2cR2PI spectroscopy of the complexes of (R+)1-phenyl-1-propanol (P_R) molecule with chiral alchools and water are reported.

¿From the excitation spectrum of the P_R molecule, already reported, it can be inferred that three different conformers are present. Their occurrence is confirmed by ab initio calculations. In the 2cR2PI absorption spectrum of the $P_R B_S$ and of the $P_R B_R$ the shifts of the most intense bands, assigned to the electronic band origin of the most stable clusters, are bathochromic. Moreover they are shifted 13 cm^{-1} one respect to the other, as already seen in 1cR2PI experiments.

The 1cR2PI wavelength scan in the $S_1 \leftarrow S_0$ region of the molecule monitoring: the 1:1 and 1:2 $P_R(H_2O)_n$clusters shows a blue shift of 90 cm^{-1} and 20 cm^{-1} with respect to the bare molecule. This indicates that in these systems the electrostatic interactions appear to overcome the actractive interactions, namely dispersion and polarization.

In table 1 IPs and dissociative appeareance potentials of of $P_R B_R$, $P_R B_S$ and $P_R H_2O$ clusters are reported together with their $D_o^{''}$ and D_o^+ energies.

The dissociation energy of $P_R B_R$ in the ground state is larger by about 360 cm^{-1} with respect to the analogous complex with $P_R B_S$. Since the pure hydrogen bond interaction should be essentialy the same in diastereomeric complexes, the measured difference between $P_R B_R$ and $P_R B_S$ bond energy can be mainly attributed to differences in attractive and repulsive dispersion forces.

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	$h\nu_1$(cm^{-1})	$h\nu_2$(cm^{-1})	$h\nu_3$(cm^{-1})	$D_o^{''}$(cm^{-1})	D_v^+(cm^{-1})
$P_R B_S$	37485±1	33160±40	35540±40	1700±40	2380±40
$P_R B_R$	37498±1	32950±40	35890±40	2060±40	2940±40
$P_R H_2O$	37663±1	33471±20	35353±40	1690±40	1880±40

Table 1: Photon energy for excitation ($h\nu_1$), threshold ionization ($h\nu_2$). and threshold dissociative ionization ($h\nu_3$), of $P_R B_R$, $P_R B_S$ and $P_R H_2O$ clusters and derived dissociation energies of fundamental ($D_o^{''}$) and ionic state (D_o^+)

A QUASICLASSICAL TRAJECTORY STUDY OF THE
Ne + H_2^+ -> NeH^+ + H PROTON TRANSFER REACTION
AND ISOTOPE VARIANTS (D_2, HD)

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The aim of this contribution is to investigate by means of the quasiclassical trajectory (QCT) method the moderately endoergic gas phase proton transfer reactions

$$Ne + H_2^+ \rightarrow NeH^+ + H \qquad \Delta D_0^0 = 0.54 \text{ eV} \qquad (1)$$

$$Ne + D_2^+ \rightarrow NeD^+ + D \qquad \Delta D_0^0 = 0.53 \text{ eV} \qquad (2)$$

$$Ne + HD^+ \rightarrow NeH^+ + D \qquad \Delta D_0^0 = 0.56 \text{ eV} \qquad (3a)$$

$$\rightarrow NeD^+ + H \qquad \Delta D_0^0 = 0.51 \text{ eV} \qquad (3b)$$
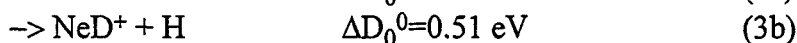
with vibrationally excited reactant molecular ions, taking into account the influence of translational energy (E_T) and using the best potential energy surface (PES) available. This proton transfer reaction has been the subject of several experimental and theoretical studies. The reaction takes places on the ground potential energy surface (PES), $^2A'$, of the NeH_2^+ system, which presents a collinear $[Ne-H-H]^+$ minimum placed along the minimum energy path connecting reactants and products. The single PES character of this system and the reduced number electrons involved allow for a very strong interaction between theory and experiment.

A quite good agreement with the following experimental data has been obtained: (a) the relative total cross sections for selected vibrational levels (v=0-4) of H_2^+ as a function of E_T (0.36-3.5 eV); (b) the relative reaction rates as a function of the vibrational levels (v) of H_2^+ (v=0-8) and D_2^+ (v=0-12) at thermal E_T; (c) the intramolecular isotope effect (NeH^+/NeD^+ ratio) from 0.4 to 3.2 eV (Franck-Condon vibrational distribution of HD^+ resulting from HD). Moreover, a good/reasonable good agreement has been obtained for the NeH^+ angular distributions for E_T=0.87-4.05 eV (Franck-Condon vibrational distribution of H_2^+ resulting from H_2). The resulting QCT E_T' distributions peak at lower E_T' values and are narrower than the experimental ones. More details on the results obtained will be presented at the meeting.

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AB INITIO GROUND PES AND QCT STUDY OF THE

O(^{1}D) + CH$_4$ -> OH + CH$_3$ REACTION DYNAMICS

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The reactions of the oxygen atom in the first excited electronic state (O(^{1}D)) with alkanes, and specially with CH$_4$, are relevant in stratospheric chemistry in the context of ozone degradation through the OH/HO$_2$ catalytic cycle. Furthermore, its highly different reactive behaviour with respect to the ground state oxygen atom (O(^{3}P)) makes the study of this kind of systems particularly interesting. Despite of the abundant experimental information available on the O(^{1}D)+CH$_4$ system, theoretical studies are very scarce. In this context, an ab initio study of the ground potential energy surface (PES) of the reaction
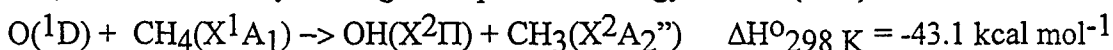
$$O(^1D) + CH_4(X^1A_1) \rightarrow OH(X^2\Pi) + CH_3(X^2A_2'') \quad \Delta H^{\circ}_{298\ K} = -43.1\ kcal\ mol^{-1}$$

has been performed using the second and fourth-order unrestricted Møller-Plesset methods with a large basis set. From the ab initio data a triatomic analytical ground PES with the methyl group treated as an atom of 15.0 a.m.u. has been derived. This PES has been employed to study the dynamics by means of the quasiclassical trajectory (QCT) method. A good agreement between the experimental and QCT OH rovibrational distributions at a collision energy of 0.212 eV with the methane molecule at 298 K has been obtained. The analysis of the microscopic reaction mechanism shows that the reaction takes place almost exclusively through the insertion of the O(^{1}D) atom into a C-H bond, due to the presence of the deep (CH$_3$)OH minimum, and the resulting trajectories may be direct or non-direct (short-lived collision complexes mainly) with about the same probability. The OH vibrational distribution arising from the direct mechanism is inverted, while the non-direct mechanism leads to a non-inverted one. There is some tendency to give broader OH rotational distributions peaking at higher N' values, particularly for the vibrational levels v'=0-1, in the case of the non-direct trajectories. The PES derived here may be used in dynamics studies under conditions where the methyl group motions are not strongly coupled to the motions leading to reaction. To the best of our knowledge this represents the first theoretical study performed on the dynamics of this reaction.

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AB INITIO GROUND POTENTIAL ENERGY SURFACE

AND QCT STUDY OF THE O(^{1}D) + H$_2$O REACTION

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The reactions of the oxygen atom in the first excited electronic state, O(^{1}D), with hydrogen containing molecules are of a great interest in various fields of chemistry. Thus, the reaction with water, is relevant in stratospheric chemistry in the context of ozone degradation processes through the OH/HO$_2$ catalytic cycle. Furthermore, the highly different reactive behaviour of O(^{1}D) respect to the ground state oxygen atom, O(^{3}P), makes the study of this kind of systems particularly interesting.

The aim of this work is to study theoretically the gas phase reactions:

$$O(^1D) + H_2O(X^1A_1) \rightarrow 2\ OH(X^2\Pi) \tag{1}$$

$$\rightarrow H_2(X^1\Sigma_g^+) + O_2(a^1\Delta_g) \tag{2}$$

$$\rightarrow H(^2S) + HO_2(X^2A") \tag{3}$$

ΔH°_{0K}= -27.09, -24.19 and 10.49 kcal mol^{-1} respectively. Reaction (1) is clearly dominant under thermal conditions and very fast, its activation energy being expected to be very small.

The study of the ground potential energy surface (PES) has been performed at the spin projected unrestricted fourth-order Møller-Plesset (PUMP4) ab initio level, with all electrons correlated, and using the 6-311G(3d2f, 3p2d) basis set. Ten saddle points, two minima (one of them corresponding to the H$_2$O$_2$ molecule) and 120 additional ab initio points have also been calculated. The theoretical geometries, frequencies and energies are in agreement with the available experimental data.

From the abovementioned ab initio data of the ground PES a single valued analytical representation of the PES has been derived, with the OH group of the water molecule treated as an atom of 17.0 a.m.u. This PES has been employed to study the dynamics of reaction (1) by means of the quasiclassical trajectory (QCT) method. A quite good agreement between the experimental and QCT OH(X$^2\Pi$) vibrational populations of the "new" OH fragment formed has been observed, although the corresponding QCT rotational distributions are hotter than the experimental ones. A detailed discussion of the results obtained will be given at the meeting.

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INFLUENCE OF THE COLLISION ENERGY ON THE O(^{1}D) + RH --> OH(X^{2}Π) + R (RH=CH$_4$, C$_2$H$_6$, C$_3$H$_8$) REACTION DYNAMICS. A LIF AND QCT STUDY

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The reactions of the oxygen atom in the first excited electronic state, O(^{1}D), with alkanes, and specially with CH$_4$, are relevant in stratospheric chemistry in the context of ozone degradation processes through the OH/HO$_2$ catalytic cycle. The influence of the collision energy on the O(^{1}D) + RH --> OH(X^{2}Π) ÷ R (RH=CH$_4$, C$_2$H$_6$, and C$_3$H$_8$) reaction dynamics has been studied, using the N$_2$O photodissociation at 193 nm as O(^{1}D) precursor and probing the OH v"=0 and 1 levels by LIF. A triatomic QCT study of the reaction with CH$_4$ on a fully ab initio-based analytical PES has also been performed, and a good agreement with the experimental OH rovibrational distributions has been obtained. Our experimental results are similar to those obtained when the O$_3$ photodissociation is used to produce O(^{1}D), as expected on the basis the available energy in products and also from the QCT calculations. The P(v"=0)/P(v"=1) populations ratio values reported for C$_2$H$_6$ and C$_3$H$_8$ in a very recent work (Wada and Obi, J. Phys. Chem. A **102**, 3481 (1998)), where the N$_2$O was also used to generate O(^{1}D), are probably largely underestimated. The rotational distributions obtained are similar to those obtained in other experiments, and a quite good agreement has been obtained for the spin-orbit and doublet lambda populations. The reaction takes place near exclusively through the insertion of the O(^{1}D) atom into a C-H bond, and the mechanism may be direct or non-direct (mainly through short-lived (CH$_3$)OH collision complexes) with about the same probability. The OH vibrational distribution arising from the direct mechanism is inverted, while the non-direct one leads to a non-inverted distribution.

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AB INITIO GROUND PES AND QCT STUDY OF THE

$Cl + CH_4 \rightarrow HCl + CH_3$ REACTION DYNAMICS

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The reaction of chlorine atom with methane is of a great interest in atmospheric chemistry as it is an important termination step in the chlorine/ozone stratospheric chain mechanism that leads to the destruction of ozone. This reaction, that involves the most abundant hydrocarbon, produces HCl which is an effective sink for Cl atoms. Due to its importance, this reaction has been studied by different experimental and theoretical methods. In this contribution, we present an ab initio study of the ground potential energy surface (PES) of the $Cl + CH_4 \rightarrow HCl + CH_3$ reaction that has been performed using the second and fourth-order unrestricted Møller-Plesset methods with the 6-311G(2df, 2pd) basis set. From the ab initio data a triatomic analytical representation of the ground PES with the CH_3 group treated as an atom of 15.0 a.m.u. has been derived. This PES has been employed to study the dynamics in the framework of the quasiclassical trajectory (QCT) method. The theoretical results have been compared with the available experimental data, obtained when the Cl atom is generated by photodissociation of Cl_2 at 355 nm, from which an average collision energy of 0.159 eV results, and the CH_4 molecule is vibrationally excited. A quite good agreement has been obtained between theory and experiment for the HCl rovibrational populations, and also for the state-specific k-k' angular distributions of the HCl(v'=1, j'=0-3) molecules produced. The microscopic reaction mechanism has been analysed taking into account the geometry and energy of the system in the strong interaction region. The reaction follows a direct reaction mode and the Cl-H-(CH₃) angle tends to substantially deviate from collinearity (average value of about 120°), although the collinear approach presents the lowest energy barrier to reaction. For the HCl(v'=0) products, the average angle shows essentially no deviation with respect to that of the global reaction, as it accounts for 81% of the total population. However, for HCl(v'=1) a shift towards higher angular values has been observed. When the rotational level of the HCl molecule is considered, a shift towards collinearity is obtained when the HCl product arises with low rotational excitation. The PES model used here may be used in dynamics studies under conditions where the CH_3 motions are not strongly coupled to the motions leading to reaction.

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FTIR Spectroscopy of Molecular Clusters in Pulsed Slit Nozzle Expansions

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Broadband characterization of the vibrational dynamics of molecular clusters using rapid scan Fourier transform infrared spectroscopy becomes feasible if sufficiently high particle densities can be maintained for the period in which an interferogram is recorded (typically 50 ms – 1 s, depending on the required spectral resolution) [1]. For this purpose, we use supersonic expansions from a pulsed slit nozzle of fairly large cross section (120 mm × 0.5 mm). High gas throughputs of about $1 \, mol \, s^{-1}$ at background pressures below 100 Pa are realized with the help of a large buffer volume ($7 \, m^3$) combined with a roots pumping system (pumping speed $2000 \, m^3 h^{-1}$). We shall present a number of examples which demonstrate the power and high sensitivity of our combined jet spectrometer system for the measurement of molecular cluster spectra [2]. For intense vibrational bands almost complete absorption of infrared radiation is achieved in a single pass. Spectral resolution is currently limited by the FTIR spectrometer to $0.1 \, cm^{-1}$ FWHM. Systematic studies of cluster distributions as a function of position relative to the nozzle, stagnation pressure and composition of the expanded gas mixture are carried out. Infrared absorption bands of dimers and oligomers as well as of solid, liquid and glass-like nanoparticles are observed. Comparison to results from quantum-chemical calculations is made. The method is competitive with and complementary to recent cavity-ring-down techniques [3].

A study of aliphatic alcohols with systematic variations of the alkyl group reveals strong influences on the clustering tendency. The effect of branching [2] and of fluorination [4] of the alkyl groups is investigated in detail. In several cases, conformational isomerism arising from the hindered rotation around single C–O bonds is observed. As an example, the table below shows tentative dimer, trimer and tetramer assignments of the OH-stretching bands for some of the alcohols studied. In cases where more than one peak is tentatively assigned to a given oligomer, only the strongest central peak position is given.

$\tilde{\nu}_{OH}/cm^{-1}$	monomer	dimer[†]	trimer[†]	tetramer[†]
CH_3OH	3686	3576(−110)	3471(−215)	3293(−393)
$(CH_3)_2CHOH$	3658	3520(−138)	3438(−220)	3261(−397)
cyclopentanol	3656	3516(−140)	3424(−232)	3266(−390)
$(CH_3)_3COH$	3644	3498(−146)	3414(−230)	3259(−385)
$(CF_3)_2CHOH$	3624	3494(−130)		3330(−294)

[†] Numbers in parentheses represent shift with respect to monomer

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New analytic technique for calculating reactive scattering cross sections from wavepacket dynamics

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In order to use wavepackets to calculate reaction probabilities an initial wavepacket is "placed" on a potential energy surface and propagated as a function of time. To analyse the wavepacket dynamics and calculate the reaction probabilities the initial momentum ditribution of the wavepacket is needed. If a small grid is used the wavepacket does not satisfy the fact that at the beginning of a reaction $A + BC \longrightarrow AB + C$ the atom A is far away from the diatomic molecule BC. To take account of this and get the "true" initial momentum ditribution, while still using a small grid, a one dimensional effective potential in R (the scattering coordinate) is generated. The wavepacket then is propagated backwards on this potential. This provides the initial momentum distribution and the shift in energy which are needed to calculate the correct reaction probabilities.

When a small grid is used and the wavepacket propagation is started at a distance $R = R_0$, not equal to infinity, the atom A affects the diatomic molecule BC at this seperation. In order to take proper account of this interaction the initial diatomic BC wavefunction is calculated in the presence of the A atom.

To analyse the wavepacket dynamics a cut is taken through the wavepacket at the analysis line, $R = R_\infty$, at each time step. The wavefunction along this cut is projected onto the final product fragment wavefunctions. These product fragment wavefunctions should be computed at $R = R_\infty$, where the atom C and the diatomic molecule AB still effect each other, rather than at infinite seperation. This also gives the shifts in energy which are used for the analysis.

Rotational state-to-state rate constants and pressure broadening coefficients for He – C_2H_2 collisions: Theory and experiment

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Converged close-coupling and coupled-states calculations were used to obtain state-to-state rate constants and pressure broadening coefficients for the collisional rotational (de-) excitation of C_2H_2 by He. The *ab initio* potential used in these calculations was previously computed by symmetry-adapted perturbation theory. The computed pressure broadening coefficients and total rate constants agree well with the available experimental data. In the experimental part of the paper stimulated Raman-pumping has been used to prepare acetylene in selected rotational states ($j_i = 2$ to 18 and $j_i = 1$ to 19 of the C≡C stretching mode). The population decay in the prepared state and the transfer to other rotational states was monitored by laser induced fluorescence. The experimental data can be described by an infinite-order-sudden power law (IOS-P) or directly compared with the *ab initio* derived rate constants. The influence of multiple collisions possible at the relatively large pressure-delay-products employed has been taken into account by simulating the rotational energy transfer with a master equation. Experimentally we obtain a total rate constant for depopulation of $k_{tot} = 10.89 \pm 0.07 \ \mu s^{-1}Torr^{-1}$ and IOS-P fitting parameters of $A = 5.58$ and $\gamma = 0.96$ in very good agreement with the *ab initio* calculated values. There we obtain $k_{tot} = 10.69 \pm 0.09 \ \mu s^{-1}Torr^{-1}$ and IOS-P fitting parameters of $A = 6.18$ and $\gamma = 0.96$. Also the experimental state-to-state rotational energy transfer constants, which vary from 5.83 to 2.32 $\mu s^{-1}Torr^{-1}$ for endothermic $\Delta j = 2$ collisions, agree very well with the *ab initio* data.

Multiconfiguration time-dependent Hartree (MCTDH) calculations of reactive and surface scattering processes

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Theoretical investigations of reactive scattering and molecule-surface scattering are performed using the multiconfiguration time-dependent Hartree (MCTDH) method, designed for efficiently propagating quantum wavepackets for multi-dimensional systems. A correction scheme for the initial wavepacket allows us to place the initial wavepacket rather close to the scattering center, thus keeping the propagation time small. This correction scheme is based on the assumption of both vibrationnally adiabatic motion and validity of a WKB description for the asymptotic in-going part of the exact time-dependent solution. The analysis of the propagated wavepacket is performed using a combined flux operator/complex absorbing potential approach.

Cumulative initial-state-selected cross section of the $H+D_2$ system are computed. Calculations are performed within the coupled states approximation on the LSTH potential energy surface. Initial states $\nu = 0, 1$ and $j = 0 - 4$ and initial translational energies up to 2.5 eV are considered. To compare with experiment, rotationally thermaly averaged cross sections are also computed[1].

Rotational and diffractive inelastic scattering of a rigid diatomic molecule from a corrugated static surface is investigated. The numerical simulations concern the five-dimensional $N_2/LiF(001)$ model system for an energy range of 60 meV to 300 meV, including a very large number of open diffractive and rotational channels. State-to-state transition probabilities as well as average energy transfer values are extracted from the wavepacket propagation [2].

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Ab initio study of the ground and low-lying electronic states of O_4

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Knowledge of the electronic structure of the O_4 system is crucial to understand the dynamics of the collision $O_2(v) + O_2(v=0)$ which has been at the center of a debate about new mechanisms to explain the ozone stratospheric budget[1]. Measurements of the total depletion rate of $O_2(v)$ show a sharp increase above a critical value of the vibrational quantum number, v , which has not been decisively explained either theoretically or experimentally[2] and recent spectroscopic studies suggest the relevance of non-adiabatic processes in the O_4 system[3]. Altough there have been several dynamical studies based mainly on the Varandas and Pais potential[4] and a recently obtained ab initio model surface[5] both for the ground triplet state, there have not been any detailed ab initio calculations performed on the ground and low-lying electronic states of O_4.
Some of the issues we have been looking at are:

a) We have found crossings between the ground electronic state of O_2 ($X^3\Sigma_g$) and the first two excited states (a $^1\Delta_g$, b $^1\Sigma_g$) at large values of the internuclear distance corresponding to highly vibrationally excited states. Recent spectroscopic studies of the Wodtke group have shown the presence of spin-orbit coupling effects between the ground and b state at total energies in good agreement with our calculations.

b) For the O_4 system the crossing must appear at the corresponding asymptotes and we have been analyzing how it is modified energetically as we approach the O_2 molecules for different orientations.

c) We are also studying the O_4 chemically bound complex and the reaction path leading to $O_2 + O_2$ and the crossings between electronic states along the path.

The relevance of our findings to experimental observations will be emphasized.

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Isotope Effects in Collisional Energy Transfer between N_2 and Excited $MuO_2(HO_2)$ Formed by Addition of Mu(H) to O_2 in the Low Pressure Regime.

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Mu is a very light hydrogen isotope with a (μ^+)-nucleus and a mass that is only one-ninth that of H. The strongly exothermic addition of Mu to O_2 requires moderator (N_2) to take up the excess energy of the highly excited MuO_2^* formed on addition, so that the product MuO_2 can be stabilized. Here, we provide a theoretical analysis of the isotope effects revealed by comparison of the low pressure limiting rate constants which were reported for the Mu and H reactions [1,2]. Assuming an exponential energy transfer, the mean transferred energy ΔE was calculated from the empirical weak collision factor β_c, the latter being the ratio of the experimental rate constant to the calculated strong collision rate constant k_0^{SC}. For this, k_0^{SC} was calculated utilizising the semiempirical potential energy surface DMBE IV.

Generally, β_c and ΔE are thought to depend upon the moderator rather than on the reaction partners, i.e. to be the same for isotopic reactants. In contrast, the results for $Mu+O_2$ show a large difference compared to $H+O_2$. Over a temperature range from 115 K to 463 K, $\beta_c(Mu)$ is one half of $\beta_c(H)$, which corresponds to the ratio $\Delta E(MuO_2)/\Delta E(HO_2) \approx 0.3$ at room temperature.

This considerable ratio, that does not appear for $D+O_2$, might be interpreted in terms of the higher frequencies of the bending and of the Mu—O-streching mode, which prevents these modes from contributing efficiently to the collisional energy transfer with the moderator.

Theoretical investigations based on trajectory calculations about the influence of the frequencies on ΔE were reported in the literature [3], while experimental confirmation was still lacking. Relating to this, μSR-experiments in comparison with those of H offer a unique test on account of the large mass ratio.

Another aspect, that has been analysed only rarely yet, but might become important for Mu, is the effect of tunneling in the low pressure regime.

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An Experimental Realization of the OH+D$_2$ →HOD+D Reaction: Providing a Pulsed Source of OH-Radicals

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The OH+H$_2$ →H$_2$O+H reaction (and its isotopic variant OH+D$_2$ →HOD+D) is of great interest as a fundamental reaction in the investigation of molecular reaction dynamics. It serves as the four-atom benchmark system since now six dimensional quantum calculations on this reaction are possible. It plays as well an important role in combustion of H$_2$ and hydrocarbons and in atmospheric physics, where this reaction leads to the formation of water. In interstellar chemistry, the reaction is believed to be responsible for the inversion of the H$_2$O maser.

In order to investigate the OH+D$_2$ reaction in a crossed beam experiment, a pulsed source of translationally hot OH radicals is necessary. At the moment, a new molecular beam set-up is tested to provide the OH-radicals. As a precursor, H$_2$O$_2$ obtained from an urea/hydrogen-peroxide compound is used in a specially modified pulsed nozzle. Translationally hot OH-radicals will be produced via photodissociation at 193nm wavelength. As the next step, the OH state distribution as well as the velocity distribution within the molecular beam will be determined via LIF. The findings of the characterization will be reported.

After the OH-source is successfully characterized, it will be applied to the OH+D$_2$ crossed molecular beam experiment, where the product D-atoms are detected via the Rydberg-tagging TOF technique. Latest results will be presented.

ACCURATE QUANTUM DYNAMICAL CALCULATIONS FOR THE N(^{2}D) + H$_2$ → NH + H REACTION

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There has been recent experimental and theoretical interest on the title reaction. A QCT study[1] on an empirical potential energy surface (PES)[1] has shown a good qualitative agreement with the experimental vibrational and rotational distributions of Umemoto's experiments[2]. Using a crossed molecular beam technique, Alagia et al.[3] measured the total DCS and product translation energy distribution for the N(^{2}D)+D$_2$ reaction at 165 and 220 meV collision energies. The forward-backward symmetric DCS may characterize an insertion process. This result has been confirmed by recent QCT calculations[3,4] on a fully *ab initio* PES[4].

We performed three-dimensional quantum dynamical calculations for the N(^{2}D) + H$_2$($^1\Sigma^+$) →NH(X$^3\Sigma^-$) + H(^{2}S) reaction[5]. We used the hyperspherical method and the recent *ab initio* PES[4] which is available. Converged results have been obtained in the 70-165 meV energy range by including all allowed Ω-components in the wavefunction expansion. We present integral and differential cross sections, as well as product angular and translational energy distributions. Work on the O(^{1}D)+H$_2$ → OH + H reaction is also in progress.

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CHEMICAL INTERACTIONS OF SUPER-EXCITED MOLECULES ON METAL SURFACES

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ABSTRACT

We present the first results of a new experimental method capable of revealing the chemical dynamics of highly vibrationally excited molecules at solid surfaces. We have measured the quantum state-resolved scattering probabilities of highly excited NO molecules at clean and O covered Cu(111) surfaces, where the incident NO was prepared in single quantum states with as much as 300 kJ/mol of energy in vibrational motion. From the dependence of vibrationally elastic and inelastic scattering on O coverage, we arrive at compelling evidence that the highly excited NO (v=13 and 15) reacts on a clean Copper surface with a probability of 0.87±0.05, more than one thousand times larger than the reaction probability of ground state NO. Despite the fact that vibrational relaxation at metal surfaces is expected to be efficient, this result shows that vibrational promotion of surface chemistry (all the way up to near unit reaction probability) is possible. Our approach provides a new experimental probe of non-equilibrium surface chemistry. We also present preliminary results on the vibrational relaxation of highly vibrationally excited molecules at solid surfaces. We observe NO in v=13 and 15 loosing up to five vibrational quanta in collisions with an O-covered Copper surface. The data indicates this vibrational relaxation occurs via a direct scattering mechanism.

Product imaging: Ion counting improvements and applications

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Ion counting and velocity mapping have been used to increase the speed and angular resolution of product imaging. Applications to the photodissociation of ozone will be discussed. The channel giving $O(^1D)$ and $O_2(^1\Delta)$ has been examined at a wide range of wavelengths. Results include the variation in vibrational distribution at these wavelengths, the orbital alignment of the $O(^1D)$, the observation that vibrationally excited ozone absorbs much more strongly than ground state ozone, and the observation of rotational resolution in the recoil velocity, leading to an improved dissociation energy for ozone. The channel giving $O(^3P)$ and $O_2(^3\Sigma)$ has also been examined at a variety of wavelengths: 226 nm, 230 nm, 240 nm, and 266 nm. The vibrational distributions obtained for the various ^3P_J products, when combined with measurements of the yields of these channels, allows us to calculate how much $O_2(v >= 26)$ is produced as a function of wavelength. Possible stratospheric consequences will be discussed.

The application of complex absorbing potentials to an invariant embedding scattering method.

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Abstract

The application to several triatomic reactions of a novel implementation of absorbing potentials on a generalized R-matrix propagation method is presented[1, 2, 3]. Specific systems chosen have been $Li + FH$, $Mg + FH$, and $H + F_2$, so that an extensive application covering a wide range of PESs has been performed[4]: it includes moderately and largely exoergic and endoergic processes, simple and involved PES, moderate to large skew angles and direct and complex-forming collisions. In all cases it is shown that the use of the absorbing potential is simple and robust, yielding correct values at a fraction of the computer's resources consumption. The best effectiveness is obtained for exothermic, direct reactions, for which up to one order of magnitude in CPU time saving is obtained. This efficiency opened the possibility for a very detailed exploration of the reactive process, in particular on those quantities strongly dependent on the collision energy. In addition, it is shown that, as previously known from a totally different numerical approach, the cumulative reaction probability can be efficiently and accurately calculated propagating the scattering solution along a very short range of the scattering coordinate.

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Rotational Energy Transfer in Collisions of NO($^2\Pi_{1/2}$, v = 2, high J) with He, Ar and N$_2$.

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Previous measurements[1,2] of the rate coefficients for total and state-to-state energy transfer from specific rovibrational levels of NO X $^2\Pi_{1/2}$ are extended to previously inaccessibly high levels of the rotational quantum number J. The measurements are based on the IRUVDR (Infrared-Ultraviolet Double Resonance) method previously described. However in the present experiments, rather than exciting NO molecules from a thermal sample, NO is formed in a non-Boltzmann distribution by photodissociation of NO$_2$ at 355 nm. This process produces NO in levels v = 0, J ≤ 40.5 [3], so that application of the IRUVDR method allows specific high J states in v = 2 to be accessed and observed. Results for total and state-to-state energy transfer from high J levels will be presented and compared with both earlier results from rotational levels and ab initio calculations.

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Charge Transfer and Energy Dissipation in Liquid Helium Nano-Clusters

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We have measured the fragmentation patterns for electron impact ionization of helium clusters with $300 < <N> < 10,000$, both for pure clusters and for clusters doped with Ne, Ar, Xe and NO. Ionization of pure helium clusters results mainly in fragmentation to He_2^+, but there are also "magic" numbers at n = 7, 10 and 14. It appears that the first "solvation shell" consists mainly of He_2^+ surrounded by twelve other atoms. However, the n = 15 species is also relatively intense compared to higher n species. The pattern shifts slowly toward higher n as the neutral cluster size increases. However, fragmentation is always much more extensive than would be expected on the basis of an evaporative energy dissipation mode. We believe that the He_2^+ fragment is ballistically ejected from the cluster on the picosecond time scale.

For ionization of helium clusters doped with a single Ar atom, we have measured the probability that the charge appears on Ar, rather than as He_n^+. This charge transfer probability is a decreasing function of cluster size. The maximum observed probability is 25%, for clusters of a few hundred helium atoms, and the probability rapidly drops to less than 1% for clusters containing more than 5000 helium atoms. Also, we find that the bare Ar^+ ion is rarely observed upon ionization of such clusters. Instead, Ar^+He_n ions, with n up to 50, are observed. The probability of observing such an ion with a given value of n increases up to n = 12, after which there is a significant drop in intensity. When the helium clusters containing two argon atoms are ionized, the chance that a fragment containing Ar^+ is observed rather than He_n^+ is about double that for clusters that contain one argon atom. In this case, by far the most probable argon containing ion is Ar_2^+. For clusters with more than 3000 helium atoms, $Ar_2^+He_n$ species are also observed, indicating complete vibrational relaxation of the Ar_2^+ unit. For the size range of helium clusters that we are studying, Ar_2^+ is also the main ion observed if the neutral cluster held 3 or 4 argon atoms.

Surprisingly, charge transfer to Ne atoms is more efficient than to Ar atoms, for smaller helium clusters. We attribute the difference to the difficulty of the final charge transfer step, for which the energy gap is three times larger for Ar than for Ne. Clusters doped with Xe undergo a different energy dissipation pathway than those doped with Ar. This is demonstrated by the fact that observation of the simple Xe^+ ion is relatively common. This is attributed to the fact that the charge transfer reaction from He^+ to Xe is exoergic enough to yield Xe^+ excited electronic states that have highly repulsive interactions with helium atoms.

PHOTOFRAGMENTS CH_3+HCO FROM ACROLEIN PHOTOLYZED AT 297 NM: DISTRIBUTION OF ROTATIONAL STATES OF HCO.

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Acrolein (C_2H_3CHO) is a resistant to photooxidation and a day- and night- time lachrymator found in Los Angeles smog. We investigate photodissociation dynamics of acrolein by detecting fragment HCO. The formation threshold of acrolein to CH_3+HCO is measured to be 298±1 nm estimated from relative yield of HCO vs. photolysis wavelength. Florescent spectra $\tilde{B}$ $^2A'$—$\tilde{X}$ $^2A'$ (0,0) of HCO were detected; the intensity is corrected for both the florescent quantum yield and the effect of axis switching to obtain the population of rotational states of HCO. Rotational states up to $N = 12$ and $K_a = 2$ of HCO were populates and the population distribution can be described according to a Boltzmann distribution at temperature 89 ± 5 K. The relative rotational population of HCO dissociated from acrolein excited to the S_1 state at photolysis energy 34 032 ± 1 cm^{-1} is obtained. The rotational energy of HCO is obtained to be ~34% of available energy. The population of K_a=1 doublet states N_1^{μ} and N_1^{l} is about equally populated unlike the case of acetaldehyde. The population distribution among the rotational states of HCO indicates that a relatively loose transition state for formation of C_2H_3+HCO. The appearance rate of HCO is measured to be faster than our experimental condition 2×10^8 s^{-1}. The Boltzmann-type distribution and small available obtained in this work energy indicate that fragmentation occurs through a surface with barrierless or an exit barrier less than 250 cm^{-1}. Our experiment results imply that radical products can be either dissociated from the S_1 or T_1 surface.

RAPID EVAPORATIVE COOLING SUPPRESSES FRAGMENTATION IN MASS SPECTROMETRY: SYNTHESIS OF "UNPROTONATED" WATER CLUSTER IONS.

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Abstract

Hydrogen bonded water clusters were formed with inert gasses adsorbed to them in a strong molecular beam expansion. Upon photo-ionization of such mixed clusters, fragmentation of the substrate water cluster ion is markedly suppressed. Experimental evidence is presented, showing that the rapid evaporation of the inert gas from the newly formed water cluster ion efficiently removes internal energy on a time scale much faster than the usual fragmentation reactions present in pure water clusters, i.e. rates of fragmentation that are normally $>10^9$ s^{-1}. This phenomenon is exploited to produce "unprotonated" water clusters, formally $(H_2O)_n^+$. Using post source decay reflectron time-of-flight mass spectrometry, the structure of the "unprotonated" water cluster ions is experimentally determined for the first time. The structure determined, $H_3O^+(H_2O)_k \bullet OH$ where the hydroxyl radical is found outside the first solvation shell of the charge, is consistent with recent *ab initio* calculations. This simple approach to the control of fragmentation in mass spectrometry appears to have promise in applications to other interesting polymeric samples, for example biopolymers.

CROSSED MOLECULAR BEAMS STUDIES ON THE CHEMICAL DYNAMICS OF $C_2(X^1\Sigma_g^+)/C_2(a^3\Pi_u)$ REACTIONS WITH UNSATURATED HYDROCARBONS

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ABSTRACT

The reactions of C_2 clusters in their singlet $X\Sigma_g^+$ and triplet $a^3\Pi_u$ ground states with unsaturated hydrocarbons are postulated to play a key role in astrophysical sources such as cometary comae, interstellar molecular clouds, and carbon stars as well as terrestrial scenarios like hydrocarbon combustion chemistry, chemical vapor deposition, and soot formation. Due to this importance of this reaction class, the kinetics of C_2 reactions with numerous saturated and unsaturated molecules have been studied. However, these investigations were limited to the decay kinetics of the C_2 species and hence the reaction mechanism together with the reaction products could not be unraveled.

In this presentation we report the first systematic studies on the chemical dynamics of C_2 cluster reactions with C_2H_2, C_2H_4, and CH_3CCH under single collision conditions employing the crossed molecular beam technique with universal mass spectrometric detection. These experiments yield the first doubly differential reactive cross section of carbon clusters and supply valuable information of the involved potential energy surfaces to form hydrogen deficient carbon containing species. In our laboratory $C_2(X\Sigma_g^+/a^3\Pi_u)$ were produced by laser ablation of graphite at 266 nm and seeding the ablated clusters in helium carrier gas. Production conditions of C_2 were optimized, and reactive scattering experiments performed at relative collision energies between 15.6 and 38.4 kJ/mol. Reactions of C_3 clusters were found not to happen at these collision energies within the detection limits of our detector. The first reactions we have looked at are those involving simple unsaturated hydrocarbons relatively to the C_2 versus H exchange channels:

$$C_2 + C_2H_2 \rightarrow C_4H + H \tag{1}$$
$$C_2 + C_2H_4 \rightarrow C_4H_3 + H \tag{2}$$
$$C_2 + CH_3CCH \rightarrow CH_2CCCC + H \tag{3}$$

Data analysis is still in progress, but our preliminary results suggest that reactions (1) - (3) proceed through addition of the C_2 to the π system of the unsaturated hydrocarbon molecules. Further, reaction (1) forms at least the linear C_4H isomer. Investigation of reaction (3) using CD_3CCH clearly show that the H atom is selectively emitted from the CH_3 group. A deeper insight in the reaction dynamics together with ab initio calculations are currently in progress.

CROSSED MOLECULAR BEAMS STUDIES ON THE CHEMICAL DYNAMICS OF CN(X²Σ⁺) RADICAL REACTIONS WITH UNSATURATED HYDROCARBONS

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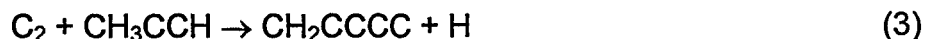*Institute of Atomic and Molecular Sciences, 1, Section 4, Roosevelt Rd., Taipei, 106, ROC*

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ABSTRACT

The chemical dynamics of $CN(X^2\Sigma^+)$ radical reactions with unsaturated hydrocarbons are of fundamental relevance to the atmospheric chemistry in Saturn's moon Titan. Its atmosphere consists mainly of N_2 and CH_4 together with minor constituents C_2H_6, C_3H_8, C_2H_2, HCN, HCCCN, and C_2N_2. Photochemically driven models of Titan's atmosphere suggest that besides cyanoacetylene a great variety of hitherto unobserved nitriles should be present as well. Therefore, we setup a systematic research program to investigate the chemical dynamics to form hydrogen deficient nitriles via neutral - neutral reactions (1) - (5) in crossed beams experiments at collision energies between 14 and 50 $kJmol^{-1}$:

(1) $CN + C_2H_2 \rightarrow HCCCN + H,$

(2) $CN + C_2H_4 \rightarrow C_2H_3CN + H,$

(3a) $CN + CH_3CCH \rightarrow CH_3CCCN + H$

(3b) $\rightarrow H_2CCCHCN + H$

(4) $CN + H_2CCCH_2 \rightarrow H_2CCCHCN + H$

(5) $CN + C_6H_6 \rightarrow C_6H_5\text{-}CN + H$

Our results show explicitly that reactions (1) - (5) are governed by indirect scattering dynamics (complex formation) and proceed via an initial addition of the CN radical to the π electron density of the unsaturated hydrocarbon to form a carbon-carbon σ bond. All H atom loss exit channels are found to be tight and located about 15 - 25 $kJmol^{-1}$ above the products. Further, a strong sideways scattering is found in reaction (5) which is less pronounced in reactions (1) - (3). These experimental data are finally compared with recent ab initio calculations.

Intramolecular- and dissociation dynamics of NO$_2$: Detailed comparison between fs/ps-experiments and quantum mechanical calculations

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Lifetimes and lifetime distributions of excited states of NO$_2$ have been measured with fs-time resolution for various excitation energies above (and below) the dissociation threshold employing a novel pump-probe technique that probes excited states and excited state dynamics of highly excited NO$_2$. In this system it has been found that intramolecular dynamics and dissociation dynamics are strongly linked and that the experiment can probe both. In a detailed investigation of the dependence of the dissociation lifetimes on rotational energy and the rotational quantum number J and K we have found a weak dependence of the lifetimes on J but at the same time that K may be conserved in the dissociation process for some time. These findings have a large impact on the prediction of unimolecular lifetimes in general. We will compare the lifetimes and lifetime distributions, their density and statistics, as well as the non expontential decays with calculated quantum mechanical resonances (3D-calculations) on a realistic potential energy surface with no adjustable parameters. We will also provide novel dynamic theoretical models from classical mechanics and quantum mechanics that account for the partial K-conservation.

NO-Ar inelastic scattering observed by high-resolution crossed-beam ion imaging

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A crossed beam apparatus with a 2-D ion imaging detector was constructed for measuring state-resolved differential cross section in reactive and inelastic scattering. Two pulsed molecular beams are crossed in a scattering chamber and the products are ionized by resonance enhanced multiphoton ionization. The velocity distribution of the ions is observed by 2D imaging (velocity mapping). A hexapole deflector is used to compensate the center-of-mass velocity of the ions and guide them to the middle of the 2-D detector, which allowed the maximum magnification possible of an ion image.

The apparatus was tested by observing the inelastic scattering of NO with Ar

$$NO\ X^2\Pi(J"=1/2,\ \Omega"=1/2) + Ar \rightarrow NO\ X^2\Pi\ (J',\ \Omega'=1/2,\ 3/2) + Ar$$
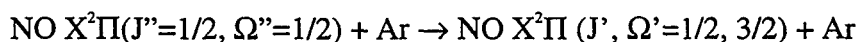
at the collision energy of 66 meV. The observed images clearly show state-dependent rotational rainbow peaks. In addition, multiple rainbow scattering was found for $J'=17/2$ $\Omega'=1/2$ for the first time in this system.

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Vector correlations in dissociative photoionization of diatomic molecules : the example of CO in the 20-35eV photon energy range

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The Vector Correlations method is developed to study dissociative photoionization of diatomic molecules (O_2, H_2, N_2, NO and CO) : spectroscopy of the ionization continuum and dynamics of the ionization and dissociation processes [1]. It consists of measuring in coincidence the velocity vectors of the produced fragment ion and photoelectron ($\bar{v}_i$, $\bar{v}_e$), by combining time-of-flight spectroscopy with position sensitive detection of both particles. The experiments are performed at the synchrotron radiation facility Super ACO in Orsay in the VUV energy range (20-40eV) where excitation of inner-valence electrons occurs. The pulsed light beam crosses a supersonic molecular jet SAPHIRS [2] at right angle. The photoelectron and the ionic fragment associated to each event are collected thanks to a uniform DC electric field in a 4Π solid angle.

For a given photon energy, the different processes are first identified and selected from the correlated kinetic energies of the electron and the ion (ε_e, ε_i). For each process, the spatial analysis of the vector correlation ($\bar{v}_i$, $\bar{v}_e$) provides in a second step the *angular distribution of the photoelectrons in the molecular frame (θ_e), for each direction of the internuclear axis (χ_i) with respect to the linear polarization* ($\bar{P}$) of the incident light [3].

For the CO molecule at hv=32eV, both the C^+ and O^+ ionic fragments are significantly formed. We present here as an example the bidimensional histogram (χ_i, θ_e) for the following process :

CO + hv($\bar{P}$)→ (CO)* →(CO)+* + e→ $C^+(^2P)$ + $O(^1D)$ + e E_D=24,3eV $\varepsilon_e \approx$ 3,4eV $\varepsilon_c \approx$ 2,4eV

χ(C+)   (deg.)
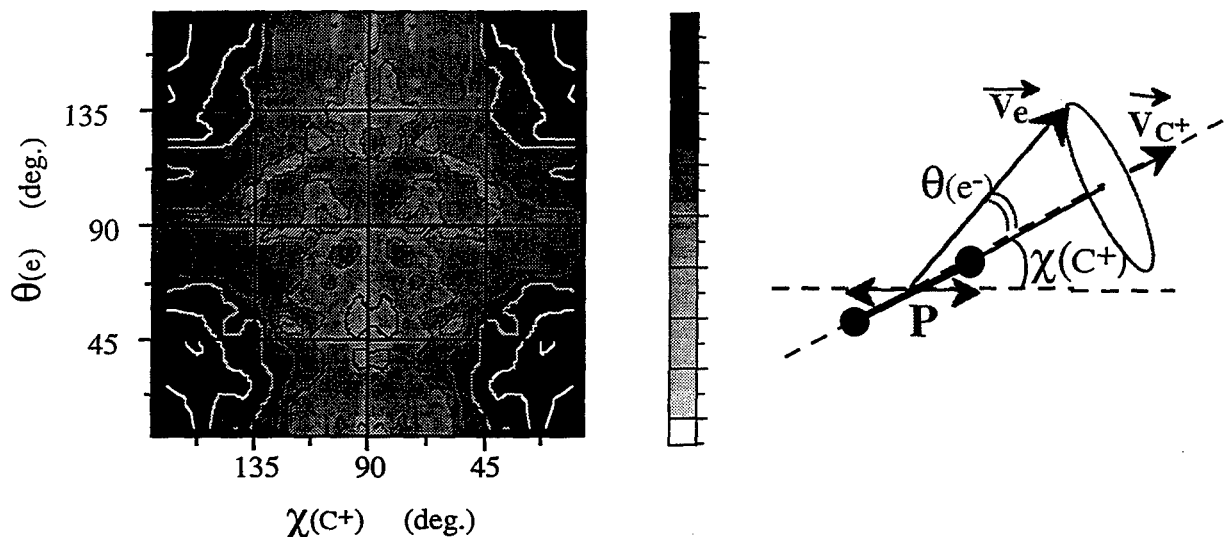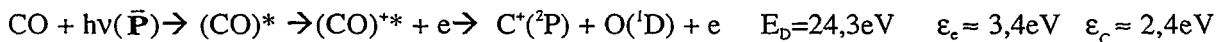
Several features characterizing this process are revealed : (i) the parallel transition dominates in the photoabsorption process ($\beta_c \approx 0,4$) (ii) the photoelectrons are emitted preferentially along the molecular axis. Features of the other processes involved will be discussed at the conference and compared to other results for this system in gas phase and adsorbed phase [4].

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Electron impact cross sections for electronic excitation of vibrationally excited O_2 to $B^3\Sigma_u^-$ state.

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In the last years a great effort has been devoted to the research on the upper atmosphere in order to clarify the mechanism of ozone depletion.

The computer codes used for the numerical simulations are mainly based on coupling between fluid dynamics models and chemical kinetics of all the elementary processes occurring in the system including, in particular, those processes leading to the formation or destruction of O_3 molecule. In this frame the photodissociation channels of the various molecular species assume a fundamental role. The photodissociation of O_2 molecule, in fact, yields to the formation of atomic oxygen, precursor of O_3 in the stratosphere, while the ozone photodissociation can lead, in the region of ultraviolet (200 - 310 nm), to the formation of vibrationally excited $O_2(v)$ molecules [1], which behave as independent chemical species.

The dissociation of $O_2(v)$ molecules, however, can be promoted also by electron collisions, and these channels in effect could play a non negligible role in the stratospheric chemistry. Inclusion of these processes in numerical codes requires an accurate knowledge of e-$O_2(v)$ collision cross sections as well as the related rate constants.

We performed, in the frame of the impact parameter method, calculations of cross sections for both excitation and dissociative processes for the dipole allowed transitions to the B $^3\Sigma_u^-$ state of O_2, the so called Schumann-Runge band, that is one of the major dissociative channels for molecular oxygen in the stratosphere, emphasising the role of vibrational excitation.

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VAN DER WAALS MINIMA ON THE POTENTIAL SURFACE OF THE OH + HCl → Cl + H_2O REACTION

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Ab initio calculations were performed up to the QCISD(T)/complete basis set limit to determine the properties of the Van der Waals complexes between OH and HCl and Cl + H_2O on the potential surfaces corresponding to the A' and A" symmetry. The A' surface correlates with the (out-of-plane) transition structure for reaction. There are two minima on this surface, one corresponding to the HO-HCl and one to the ClH-OH arrangement. The minimum located on the reactant side of the A" surface, the HO-HCl structure is the deepest well in this system. Minima on the product side were also located and studied, as well as the barrier height at the QCISD(T)/CBS level. The energetics and the properties of the Van der Waals type complexes will be discussed, together with the implications of the existence of complexes in kinetics and spectroscopy.

Zero electron kinetic energy and threshold photodetachment spectroscopy of Ar_nCl^- and Xe_nI^- clusters (n=1-15)

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Ar_nCl^- and Xe_nI^- clusters and the corresponding open-shell neutral complexes have been investigated by anion zero electron kinetic energy (ZEKE) and partially discriminated threshold photodetachment (PDTP) spectroscopy. The ZEKE spectra of the $ArCl^-$ and XeI^- diatomics show well-resolved progressions in the low-frequency vibrations of the anion and the neutral diatomic complexes; this allows us to construct accurate model potential functions for the anion and the neutral $X1/2$, $I3/2$ and $II1/2$ states. Studies of larger clusters provide size-dependent electron affinities (EAs) and electronic state splittings between the neutral X, I and II states. Cluster minimum energy structures have been determined by means of simulated annealing molecular dynamics calculations using the $Ar-Cl^{(-)}$ and $Xe-I^{(-)}$ pair potentials and various nonadditive terms. The EAs calculated without many-body effects overestimate the experimental EAs by up to 3000 cm^{-1}. Repulsive many-body induction in the anion clusters is found to be the dominant nonadditive effect. In addition, the attractive interaction between the halide charge and the rare gas exchange quadrupole plays an important role. Unique global minimum energy structures for the anion clusters arise from the influence of the many-body terms, yielding e.g. Xe_nI^- arrangements with a closed shell of xenon atoms around the iodide anion for the clusters with $n = 12-14$.

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Fine Structure Relaxation of Aluminium by Atomic Argon between 30 and 300 K

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This paper reports the first measurements at low temperatures (44-137 K) of rate coefficients for collision induced spin-orbit transitions, using a CRESU (french acronym for Cinétique de Réaction en Ecoulement Supersonique Uniforme) apparatus coupled with pulsed laser photolysis and laser-induced fluorescence techniques. A theoretical modelization of the Al-Ar system has been developed in the 30-300 K range, that reproduces the temperature dependence.

The CRESU technique is a SWARM technique, in which a true thermodynamic temperature is reached. The low temperatures are achieved by the supersonic expansion of a buffer gas, here argon, through a Laval nozzle. Each nozzle is calculated for a specific buffer, and generates a uniform supersonic flow whose temperature, density, and velocity are fixed by the shape of the nozzle. The density of the flow, typically a few 10^{16} cm^{-3} is high enough to ensure thermal equilibrium by collisions. The aluminium atoms have been produced in the $^2P_{1/2}$ and $^2P_{3/2}$ doublet ground state by photolysis of trimethylaluminium (TMA) using a frequency quadrupled Nd:YAG laser (75 mJ, 266 nm). The Al atoms were then monitored by LIF using the $(3s^24s)$ $^2S_{1/2}$- $(3s^23p)$ $^2P_{1/2}$ and $(3s^24s)$ $^2S_{1/2}$- $(3s^23p)$ $^2P_{3/2}$ at 394.40 nm and 396.15 nm respectively. A MOPO 730 laser provided probe laser radiation. It has been stated that both excitation and relaxation rates have a positive temperature dependence. The excitation (respectively relaxation) rate constant is 0.15×10^{-12} cm^3 s^{-1} (respectively 1.63×10^{-12}) at 53 K and 2.76×10^{-12} cm^3 s^{-1} (respectively 4.48×10^{-12}) at 137 K.

The quantum collisional treatment employed to calculate cross-section and rate coefficient between 30 and 300 K uses the Mies formalism. In order to build up the interatomic potential, a hybrid methodology has been used: a supermolecular CASSCF (Complete Active Space Self-Consistent Field) calculation of each electronic state is combined with a perturbative treatment of the polarization energy expressed through terms of C/R^n. As no other theoretical nor experimental result exists on the $A^2\Sigma^+_{1/2}$ state of AlAr, this work presents the first characterization of this state.

Vibrational Energy Transfer at Extremely Low Temperatures:
Collisional deactivation of highly vibrationally excited toluene at temperatures down to 40 K

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The deactivation of large molecules containing large amounts of vibrational energy has been studied by a number of complementary techniques[1-4] in recent years. A common feature is the preparation of an aromatic hydrocarbon with a large and well-defined amount of vibrational energy by laser excitation to the first excited singlet state followed by rapid internal conversion to generate highly vibrationally excited molecules in the electronic ground state.

In the group of Troe, Hippler and co-workers[2] used changes in ultraviolet absorption to follow the subsequent relaxation of these molecules, while Luther and co-workers[3] have developed the so-called 'kinetically controlled selective ionisation' technique, which, it is claimed, has the advantage of being self-calibrating. Barker and co-workers[4] have used time-resolved infrared emission, employing an analysis based on the assumption that the vibrational energy is distributed statistically amongst the modes of the molecules. The goal of all these methods is to yield an estimate of the average energy transferred per collision with partner M, $<\Delta E_{vib}>_M$, and how this quantity varies with the vibrational energy E_{vib}.

The principal aim of the present experiments is to examine the dependence of $<\Delta E_{vib}>_M$ vs. E_{vib} on the temperature of the bath gas. To this end we have implemented the experimental method of Barker and co-workers in the Birmingham CRESU (Cinétique de Réaction en Ecoulement Supersonique Uniforme) apparatus. This provides a fully thermalised environment for studying collisional processes at extremely low temperatures, with He, Ar and N_2 bath gases.

We will report measurements on the relaxation of highly vibrationally excited toluene, prepared via excitation and subsequent rapid isomerisation of cycloheptatriene. Experiments have been performed using laser wavelengths of 308 nm ($\sim$44,000 cm^{-1} initial vibrational energy) at room temperature and 248 nm ($\sim$52,000 cm^{-1}) over the temperature range 298—40 K. To our knowledge these are the first such measurements at low temperatures.

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Construction of accurate potential energy surface for three-body system by interpolation with reaction path weight

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We present an accurate method to construct molecular potential energy surfaces for 3-body reaction system which is suitable for state-to-state quantum scattering calculations. A modification has made to the interpolation method with reaction path weight, previously we proposed[J. Chem. Phys. **106**, 1003 (1997)] by replacing the inverse coordinates by exponential coordinate. This simple modification improves quality of the PES significantly at asymptotic and quasi-asymptotic region which enable to determine ro-vibrational quantum states accurately. This modification also saves large number of data points for the interpolation. In order to demonstrate our new scheme, interpolated PESs have been constructed for the $Cl + H_2 \rightarrow HCl + H$ reaction using analytic LEPS and on the the QCISD/6-31G** *ab initio* level. Classical and quantum dynamics calculations are performed both on the LEPS surface and on the interpolated surface. The dynamics results both partition energy into various degrees of freedom and state to state cross-sections are in excellent agreement for both surfaces.

Selective Infrared Multiphoton Dissociation of Silane

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Abstract

Silane is a widely used component in semiconductor industry, since the reactive fragments SiH_x can be produced out of it in well controlled, chemically clean environment. Further reduction of electronic device dimensions, growth of advanced structures, including use of different isotopes and new materials, requires precisely controlled, high quality film growth at lower deposition temperatures. This drives interest in new deposition techniques, and laser assisted chemical vapor deposition (LCVD), based on infrared multiphoton dissociation (IRMPD) of polyatomic molecules is one of the alternatives. Dissociation of SiH_4 therefore is a primary step in any deposition process. A number of publications devoted to silane decomposition at relatively high gas pressures using CO_2 lasers indicate that collisions are essential for the SiH_4 dissociation. However, still little is known about collision-free IRMPD of silane. This knowledge would be a key, for instance, for developing a new LCVD process combined with molecular beam epitaxy techniques, where the sample pressure is low and no collisions occur.

Our experiments use a two-laser technique to do collision-free, isotopically-selective IRMPD of silane. In the first step of this approach, we preexcite SiH_4 molecules to the first SiH stretch overtone level with a near-IR laser, selecting molecules with a single Si isotope. We then achieve IRMPD of only the preselected molecules using a line-tunable, home-made NH_3 laser pumped by a TEA CO_2 laser. By optimization of the energy, fluence and wavelength of the dissociating laser it is possible to achieve high dissociation yield for vibrationally preexcited molecules without significant dissociation of ground state molecules. Since the preexcitation step is selective for a particular silicon isotope, the overall dissociation process maintains a high degree isotope selectivity.

Calculation of State-to-State Cross Sections and
Rate Coefficients for $H_2(v,j)$ + $H_2(v',j')$

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Three dimensional quasiclassical trajectories on the chemically accurate potential energy surface of Keogh, Boothroyd, Martin and Peterson for H_2 + H_2 are used to determine converged state-to-state cross sections and rate coefficients for transitions among the (v,j) states of molecular hydrogen as the result of collisions with other hydrogen molecules. In this paper are presented the preliminary results for those (v,j) states with internal energy of less than 1 eV. Also discussed are issues in determination of threshold to energy transfer, microscopic reversibility, the extension of the calculation to all combinations of (v,j) states of the $H_2(v,j)$ + $H_2(v',j')$, and implications for master equation studies of shocked H_2 in conditions representative of star formation regions of the ISM.

Dissipative quantum dynamics in systems with strong vibronic coupling: an approach based on system-bath separation

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The proper description of the quantum dynamics of polyatomic systems is a fundamental problem in theoretical chemistry and molecular physics. Due to the exponential increase of the numerical effort with dimensionality, the accurate solution of the time-dependent or time-independent Schrödinger equation is in general infeasible even for molecular systems with only a very moderate number of atoms. However, many important effects in molecular dynamics, e.g. energy dissipation, are a consequence of the coupling of many different degrees of freedom. Thus, the development of approaches which can account for such effect is very important. Recent approaches typically separated the complete system into two subsystems. One subsystem, called *system* in the following, includes the most important coordinates which have to be treated accurately including quantum effects. The other subsystem, called *bath* in the following, includes the remaining coordinates and is treated more crudely. (Mixed quantum-classical approaches, for example, treat the *system* by quantum mechanics and the *bath* by classical mechanics). The description of the coupling between the *bath* and the *system* is the central problem of this type of treatment. Different schemes have been employed for this propose: Ehrenfest (or mean field or Hartree) type couplings, surface hoping approaches and perturbative descriptions based on the Nagajima-Zwanzig decomposition. The present work tests the applicability of a reduced density matrix approach based on Nagajima-Zwanzig projection for the description of absorption spectra of molecules with a conical intersection between the relevant potential energy surfaces.

To this end, the quantum dynamics of the pyrazin molecule after photoexcitation into the vibronically coupled S_1, S_2 states is investigated. A complete microscopic description of the system dynamics is given; all required parameters are directly derived from a Hamiltonian which incorporates all 24 vibrational modes and the three electronic states. The complete system is separated into a inner *system* which consists of 4 vibrational modes and the three electronic states and a *bath* which is made up by the 20 remaining vibrational modes. For the absorption spectrum, good agreement between the calculated spectrum and the experimental one is found. Qualitatively different dissipation effects found in the S_1 and S_2 bands can be properly described by this approach.

Vibrational relaxation in pyridine upon supersonic expansion

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The rotational spectra of four vibrational states (ring deformations) of pyridine have been assigned and measured in a supersonic expansion. The intensities of the lines of the vibrational satellites with respect to the ground state depend on the kind of carrier gas, backing pressure, pyridine concentration and symmetry of the rotational and vibrational states. Several rotational transitions of the vibrational satellites have also been measured in a stationary cell to complete the spectral assignment.

Semiclassical collision dynamics with multiple potential surfaces: the $H(1^2S) + N_2^+$ example

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A simple nonadiabatic process, the collision between an atom and a diatomic omonuclear molecular ion giving rise to different electronic states of the ionic fragment, is considered for the case of the triatomic system N_2H^-, in the energy range of $3-40eV$. New correlated PES, originating from a previous full-dimension MRDCI calculation, are employed and the dynamical calculations on these surfaces are performed by applying the semiclassical multichannel S-matrix in its recent refinements. The collision is studied in a simplified approach where the system remains fixed in the collinear arrangement. The dynamical coordinate is the distance between the H projectile and the N_2^+ center of mass while the N_2^+ vibrations are included *a posteriori* in a parametric scheme. Firstly the conditional probabilities for the nonadiabatic processes involved are extracted from the computed S-matrix and then probabilities at different impact parameters are obtained. The corresponding total cross-sections for the two main processes considered, $N_2^+(1^2\Sigma_g^+) + H(1^2S) \rightarrow N_2^+(1^2\Sigma_u^+) + H(1^2S)$ and $N_2^+(1^2\Sigma_u^+) + H(1^2S) \rightarrow N_2^+(2^2\Sigma_u^+) + H(1^2S)$, are finally computed. The nonadiabatic cross-sections reveal that the formation of N_2^+ in its lowest excited state is largely preferred. An immediate application of this theoretical work is suggested in order to stimulate and direct further ion-molecule experiments on the title system.

Hydrogen atoms at metal surfaces: Potential Energy Surfaces and Quantum Dynamics

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The possible processes occurring when an H atom approaches a transition metal surface are here investigated. Firstly, the electronic structure aspects are treated and the Potential Energy Surfaces of the different systems are obtained, by means of a set of First-Principles, Density Functional calculations based on a pseudopotential, plane-waves formalism.

These results will be the starting point for performing a set of quantum dynamical, time-dependent calculations for the scattering of Hydrogen atoms from these surfaces and for the relative chemisorption mechanism.

Control of quantum interferences in time-resolved, two-color, resonant four wave mixing (TC-RFWM)

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Diagrammatic perturbation theory and spherical tensor formalism are used to model the signal observed in time-resolved, two-color resonant four-wave mixing (TC-RFWM). An analysis using the Liouville formalism illustrates how TC-RFWM can be used to perform state-selective quantum beat spectroscopy in three level systems by controlling three experimental features:

1) the excitation scheme for the matter-field interactions,
2) the time-ordering of the input laser pulses, and
3) the polarization state of each of the input laser pulses.

The beats appear as a temporal modulation in the amplitude of the coherent light produced by the mixing process and can be understood as being due to the quantum interference between different Liouville-space pathways in the laser-induced evolution of the material density operator. New photons are, therefore, coherently produced by the input laser pulses which selectively prepare specific superposition states in the medium. The model successfully explains the properties of hyperfine quantum beats observed in time-resolved TC-RFWM in nitric oxide.

The ability to selectively prepare wavepackets in the medium whose evolution is determined by the quantum interference between specific Liouville pathways suggests that TC-RFWM could be useful in three-pulse, temporal control of reaction dynamics.

Internal energy of neutral ammonia clusters scattered off LiF(100)

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The scattering of small ammonia clusters of LiF(100) is studied. A supersonic expansion of ammonia seeded in He produces a beam of predominantly small clusters with a uniform kinetic energy of about 285 meV per monomer molecule. The mass distribution of the clusters in the jet and in the scattered flux is measured by a reflecting time-of-flight mass spectrometer via single photon photoionization with fixed frequency (hν = 10.49 eV) and tunable (hν = 8.7 to 9.8 eV) VUV laser radiation. While in the incident beam $(NH_3)_n$ clusters up to n = 65 can be observed, the mass spectrum of the scattered flux contains only a few small clusters up to n = 4. Kinetic energy and angular distributions have been measured for monomer fragments and up to $(NH_3)_2NH_4^+$. For low kinetic energies (when seeded in Kr) and for increasing fragment size the thermokinetic model [1] fits the observed distributions quite well, which is no longer the case for clusters seeded in He.

The internal energy of scattered cluster fragments is obtained from the photoionization efficiencies (PIE) of these molecules, measured as a function of photon energy. PIE curves of homogeneous and clusters protonated upon photoionization up to n = 8 have been measured for cold clusters in the incoming beam. For scattered fragments the signal to noise ratio was sufficient only for clusters up to n = 4. At photon energies below the appearance potential [2] the PIE curves decay exponentially. A direct Boltzmann fit to the decay curves yields the internal energy of scattered cluster fragments. While for the incident clusters internal temperatures between T_{cl} = 33K and 8K, decreasing with increasing cluster size, have been observed, the scattered fragments show internal energies larger than 100 meV. Since the detection of the fragments occurs about 50μs after scattering, very hot clusters may have been cooled by evaporating one or more monomers.

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A Systematic Series of Potential Energy Surfaces for the H + H$_2$ System Appropriate for the Study of the Dependence of Dynamical Quantities on Surface Quality

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A hierarchical family of analytical potential energy surfaces has been developed for the H + H$_2$ system. *Ab initio* calculations of near full CI quality (within 1 μE_h) were performed for a grid of 3913 points. Surfaces were fit for the estimated complete basis set (CBS) limit, as well as for the aug-cc-pVDZ, aug-cc-pVTZ, and aug-cc-pVQZ basis sets using a robust new functional form; the RMS fitting errors were below 0.005 kcal.

The *ab initio* energies were decomposed using a BSSE corrected many-body scheme. The estimated CBS energies were obtained using exact one- and two-body components and a three-body component that was extrapolated assuming that it converged at the same rate as the sum of the two-body components. The accuracy of this powerful new extrapolation procedure was assessed by comparing estimated and calculated aug-cc-pV5Z energies on a grid of 112 points and the mean error resulting from basis set incompleteness was estimated at below 0.01 kcal. Thus, the errors from fitting, correlation treatment, and basis-set incompleteness for the new CBS surface are now all significantly below those resulting from nonadiabatic effects.

Accurate quantal calculations[1] of D + H$_2$ rate constants and H + D$_2$ cross sections have been calculated for our new hierarchical family of H$_3$ potential energy surfaces and are compared to results with four previously reported potential energy surfaces (LSTH, DMBE, BKMP, and BKMP2). The disagreement between theory and experiment for all of these previous surfaces exceeds 30% for the rate constants at 1500 K, and the low-temperature rate constants for two of these surfaces differ by about a factor of two from the experimental values. Curiously, the potential surfaces that predict the best thermal rate constants provide the poorest agreement between theory and experiment for low energy H + D$_2$ $\rightarrow$ HD + D cross sections. The results for our new hierarchical series of surfaces will be used to assess the sensitivity of dynamical properties to the quality of the potential energy surface.

[1] S. L. Mielke, D. W. Schwenke, D. G. Truhlar, B. C. Garrett, and K. A. Peterson

Detection of HCO as a Reaction Product or a Photoproduct by CRD

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$$O(^3P) + RCH=CH_2 \longrightarrow RCH_2\cdot + \cdot CHO$$
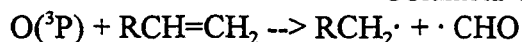
The experiments are carried out with pulsed lasers irradiating a flowing mixture of the alkene and an $O(^3P)$ precursor, usually SO_2 or NO_2. There are special problems in the detection of CHO in such a system. The spectroscopy of CHO has 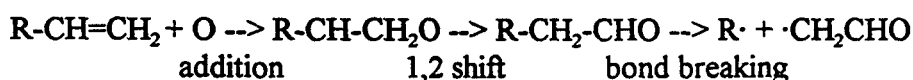normally been studied by using the $X^2A \longrightarrow B^2A'$ transition either for LIF or as the first step of a 1+1 REMPI process. However, SO_2 absorbs and fluoresces strongly in the B-X region of CHO. NO_2 reacts extremely rapidly with CHO. The X and A states are a Renner-Teller pair and consequently the fluorescence yield following the A-X transition is only about 10^{-4}. CHO must therefore be detected by absorption in the red and the cavity ring down (CRD) technique is ideal for this purpose.
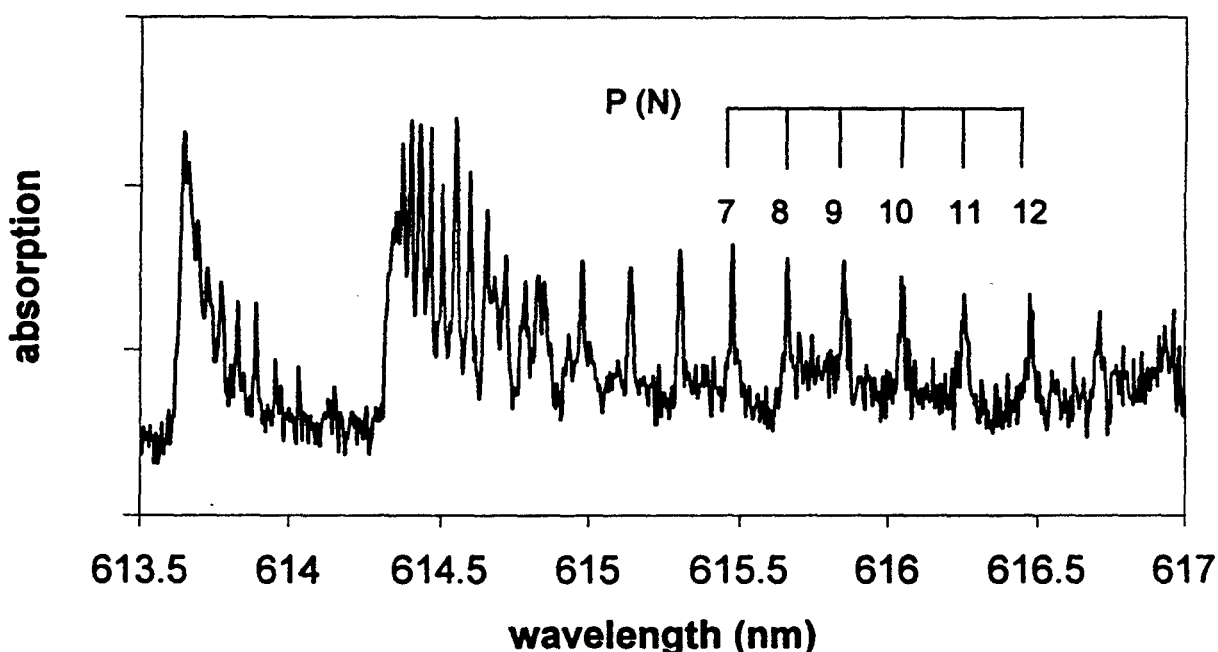
The CRD spectrum shown in the figure is of CHO from the reaction of O atoms with ethylene Although a number of other alkenes were tested, only ethylene (71%) and propylene (8%) were found to yield CHO. An explanation is that after addition of the O atom to the double bond a H atom shifts forming a hot aldehyde molecule in which the C-C bond between carbon atoms 2 and 3 is broken preferentially to that between carbon atoms 1 and 2.

$$R\text{-}CH=CH_2 + O \longrightarrow R\text{-}CH\text{-}CH_2O \longrightarrow R\text{-}CH_2\text{-}CHO \longrightarrow R\cdot + \cdot CH_2CHO$$
$$\text{addition} \qquad\qquad 1,2 \text{ shift} \qquad\qquad \text{bond breaking}$$

Other sources of H(D)CO were the photodissociation of $CH(D)_3$ $CH(D)O$ and $H(D)COOH$. An earlier finding was that the $O(^3P)$ + ethylene rreaction releases more H atoms than the $O(^3P)$ + deuteroethylene reaction releases D atoms. In confirmation we find that the reaction generates more DCO from deuteroethylene than HCO from ethylene.

Collision Energy Spectroscopy of the $H + D_2 \leftrightarrows HD(\nu = 0, j) + D$ Reaction

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A striking feature of recent studies of atom-diatom reactive scattering processes is the marked dependence of the reaction dynamics on collision energy. As the collision energy is changed by a fraction of an electron volt, the mechanism of reaction may change from direct to complex-forming[1], from adiabatic to diabatic[2], or from insertion to abstraction[3]. These studies suggest that a high-resolution measurement of the energy dependence of a bimolecular collision could reveal a rich spectrum that would shed light on the varied mechanisms that contribute to reactivity. Until now, state-to-state differential cross sections of bimolecular reactions have been measured at only a few discrete collision energies and, with one exception[4-6], at a collision energy resolution of no better than 5% of the collision energy. Here we present data taken with an apparatus that has the ability to measure state-to-state and scattering-angle-dependent cross sections of reactive scattering processes with a resolution of 0.8% of the collision energy. This precision is roughly equal to that of the best (0.6%) ever reported in a measurement of the state-to- state cross section of a bimolecular reactive scattering process[7] . The technique presented here is unique in its combined high collision energy resolution, applicability to a wide variety of reactions, and ability to study the state-and- scattering-angle dependent dynamics of a reaction as a continuous function of energy. In this study we apply our new technique to the study of $H + D_2 \leftrightarrows HD(\nu = 0, j) + D$ reactive scattering at $1.275 \pm 0.011eV$.

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The Hydrogen Exchange Reaction: Experimental and Theoretical Cross Sections and the Influence of the Geometrical Phase Effect.

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The hydrogen exchange reaction has now been studied over seven decades and still serves as a model system to develop theoretical methods to calculate the dynamics of chemical reactions. In recent years high resolution experimental results as well as fully converged 3-dimensional quantal calculations have become available for this prototype chemical reaction, both of them allowing a very detailed comparison between experiment and theory.

The $H + D_2(v = 0, j = 0) \rightarrow HD(v', j') + D$ isotopic variant has been investigated experimentally by determining rovibronically state resolved differential cross sections for a wide range of collision energies: from near the threshold up to slightly above the minimum energy for the conical intersection of the two lowest potential energy surfaces ($0.52 \leq E_{col} \leq 2.67$ eV). In comparison with theoretical results the high resolution data obtained in a crossed molecular beam experiment enabled the assessment of both the theoretical methods to calculate the dynamics and the underlying potential energy surfaces used.

The possible influence of the first excited electronic state on the dynamics has been discussed intensively in recent years. In particular the Geometric Phase effect due to the conical intersection has been predicted to become important even at relatively low energies. Detailed experimental investigations as well as a quasiclassical trajectory study were carried out to estimate the contribution of this effect to the cross sections.

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Analytical potential energy surface and scattering calculations of Cl + CH$_4$

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One of the present challenges of the chemical reaction theory is the development of methods to model accurately polyatomic reactions involving more than four atoms, such as the reaction of chlorine atoms with methane, $Cl(^2P)+CH_4 \rightarrow HCl+CH_3$. This reaction has been the aim of innovative experiments by Zare *et al.* [1]. They made chlorine atoms react with vibrationally excited methane and, using the technique of core extraction, measure the differential cross section for each HCl rovibrational state.

Nyman *et al.* [2] carried out reduced dimensionality quantum scattering calculations using the Rotating Line Approximation (RLA), where CH$_4$ is treated as a pseudo-diatom so that the reaction becomes $QH(v) + Cl \rightarrow Q + HCl(n)$ (Q = CH$_3$). They used a LEPS potential energy surface. There is also another analytical potential energy surface by Espinosa-Garcia and Corchado [3], obtained modifying a previous surface for the H + CH$_4$ reaction.

We have assembled a new analytical, full-dimensional potential energy surface (PES) for the Cl + CH$_4$ reaction. The formulation of the PES is in terms of a many-process expansion in the bond order space [4]. The PES has been fitted to reproduce the *ab initio* results of Truong *et al.* [5]. The analytical PES exactly reproduces the properties of the reactants, products and transition state. There is a classical barrier of 7.9 kcal/mol and the reaction is endothermic by 6.7 kcal/mol (without zero point energy). The PES is smooth, without any spurious structure and symmetric with respect to the permutation of hydrogen atoms.

On this new PES, we have run approximate quantum scattering calculations using the Rotating Bond Approximation (RBA). This method has already been applied to the $O(^3P)+CH_4 \rightarrow CH_3+OH$ reaction [6]. The RBA treats explicitly the umbrella vibrational modes of CH$_4$ and CH$_3$, the rotational states of CH$_3$, and a local C–H stretching coordinate and the Cl–H stretching to describe the bonds breaking and forming. The state-to-state reaction that can be described explicitly is then $Cl + CH_4(s, u, b) \rightarrow CH_3(u', j') + HCl(v')$.

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Coulomb explosion imaging and the CH_2^+ molecule

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ABSTRACT

It has been conjectured, on the basis of an interpretation of data obtained using the Coulomb explosion imaging (CEI) method, that there is a large nonadiabatic contribution to the low-lying CH_2^+ wavefunctions beyond that which comes from the Renner effect. We have calculated the energies of the lowest lying excited electronic states and find, in agreement with results already in the literature, that the excited electronic states of CH_2^+ are at much too high an energy (greater than 6 eV) for such nonadiabatic interaction to be significant. To compare with the results of the CEI method we calculate here the Boltzmann averaged bending angle distribution using our previously calculated *ab initio* potential energy curves of the pair of Renner interacting ground state potentials, and we make full allowance for the Renner effect. We find that the CEI method leads to a distribution that is significant over a wider range of bending angles than that obtained from our *ab initio* wavefunctions. This difference is too large to explain as being due to an error in the *ab initio* potential energy surfaces, and we point out two effects that could change the bending angle distributions inferred from a Coulomb explosion image; these provide an alternative way of rectifying the discrepancy.

A quantum model Hamiltonian for scattering calculations on $X+YCZ_3 \rightarrow XY+CZ_3$ reactions.

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Quantum scattering theory can now a day be applied to treat four-atom reactions with no dynamical approximations. However, these calculations are still quite involved and demand a lot of computing time. On the other hand, it has been shown that reasonable accurate results can be obtained with approximated but much simpler theories. Therefore, the problem we face now is how to use all the knowledge we have got from the study of four-atom reactions, to develop theories that allow the quantum treatment of more complex systems.

In this poster we present a model Hamiltonian to treat a reaction like:

$$X + YCZ_3 \leftrightarrow XY + CZ_3, \qquad (1)$$
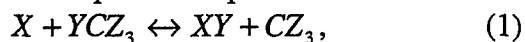
where the CZ_3 group has C_{3v} symmetry. The main assumption of the model is that CZ_3 maintains its symmetry throughout the reaction. With this approximation, a quantum Hamiltonian is derived from first principles.

This model Hamiltonian is still quite complicated to be used in scattering calculations. However, a whole hierarchy of further approximations can be applied to it, giving place to a number of different models. We present some of these more simplified models and we compare them with the Hamiltonian for a four-atom reaction and with Hamiltonians that have already been used to treat reactions like (1). Finally, we present some preliminary results obtained in the study of the reaction $O+CH_4 \rightarrow OH + CH_3$ using one of these more simplified models.

Transition state spectroscopy via infrared excitation

of Li···HF and Li···DF van der Waals precursors

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The photoinitiated reactions after infrared excitation from the LiHF and LiDF complexes in the reactant valley are studied as an extension of a recent communication[1]. For LiHF two broad bands, associated to the $\Delta v=1$ and 2, are obtained at which the probability of forming LiF products is very high, $> 90\%$. For LiDF the $\Delta v=1$ transforms in several narrow resonances, and some of them are supported by the barrier separating reactants and products valleys. Even at this resonances the reaction probability is relatively high, being about 30% at the lowest of them increasing rapidly to $> 90\%$ with increasing energy, and implies the tunneling through the barrier. The reason for the high efficiency in the photoinitiated reaction is that the main excitation correspond to the HF (or DF) stretch within the complex, which is the "active" mode for the reaction since these systems presents a late barrier. These results are very different from those obtained in a Li+HF or Li+DF collisions at the same total energies[2], for which the reaction probabilities are much lower because such excitation of the HF mode is unlikely to occur during the collision.

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Evaporation dynamics in the aniline-Ar_n van der Waals clusters

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The evaporation dynamics of the aniline-Ar_n clusters has been investigated from a theoretical point of view through the analysis of molecular dynamics (MD) simulations done in the microcanonical ensemble. Different aspects of this process have been analysed as a function of the internal energy : kinetic energy release, lifetime of the parent cluster, isomer populations in the product cluster. In particular, a sensitivity of the calculated kinetic energy release to the phase transition in the product cluster has been clearly demonstrated [1].

Unfortunately, MD simulations can only be done on the ns time scale. Then an altervative approach has been used : the exact classical densities of states of the clusters involved in the dynamics have been calculated from the multiple histogram method [2] and the statistical phase space theory (PST) has been used. This statistical approach allowed us to extract valuable informations in the μs time domain. Consequently, these theoretical predictions have revealed to be very useful to analyse the experimental results recently obtained in our group by resonant two-color two-photon ionization [3] :*i.e.* the shifts of the ionisation potential and of the $S_1 \leftarrow S_0$ electronic transition as a function of the cluster size (up to about 35 Ar atoms). In the mass spectra, a strong abundance of the aniline-Ar_{22} cluster has been clearly observed in conditions where the energy deposited in the ions is very small, and thus the mass spectra intensities reflect populations in the neutral clusters.

The temperature of the clusters at the end of the evaporative cooling has been calculated in the PST framework for different cluster sizes. For this temperature range, the isomerisation dynamics of the aniline-Ar_n (n=17-25) clusters has been studied by MD simulations. A strong entropic effect has been put into evidence around the cluster size $n=22$. A statistical model , taking into account the local densities of states in the parent and product clusters, confirms the strong abondance of the aniline-Ar_{22} cluster.

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Potential energy surface and quasiclassical trajectory studies of the N(^{2}D) + H$_2$ Reaction

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We present global potential energy surfaces for the 1 A" (ground) and 1A' (first excited) states of NH$_2$ based on application of the reproducing kernel Hilbert space interpolation method to high quality *ab initio* (multi-reference configuration-interaction) results. Extensive quasiclassical trajectory calculations are performed on these surfaces to study the N(^{2}D) + H$_2$/D$_2$ reaction dynamics. We find that the lowest energy reaction paths on both surfaces are of C$_{2v}$ symmetry, with the 1A" barrier being 1.9 kcal/mol and the 1A' barrier being about 1 kcal/mol higher. These results are in contrast to what was obtained by Kobayashi, Takayanagi, Yokoyama, Sato, and Tsunashima (KTYST) for the 1A" using a somewhat lower level *ab initio* method, where the linear geometry saddle point is of lowest energy. As a result, the new NH$_2$ surfaces exhibit an insertion mechanism, while the KTYST surface shows an abstraction mechanism. The new 1A" surface yields product distributions that are typical of an insertion mechanism, and the resulting product vibrational and angular distributions are in good agreement with experiment.

Torsion-Vibration Coupling In Methanol

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The rate of intramolecular vibrational relaxation (IVR) of high frequency stretches is correlated with the presence of a nearby low-barrier torsional degree of freedom. This correlation is thought to arise from the coupling of the extremely anharmonic torsional coordinate with other vibrations. Experimental determinations of two torsion-vibration interactions in methanol are presented:

(i) High resolution spectra of the C-H stretch fundamentals show inverted torsional tunnelling behavior for the v_2 and v_9 bands. A local mode analysis yields the parameter $\mu=12.9$ cm-1 that quantifies the coupling between the C-H stretches and the torsion. *Ab initio* calculations up to the MP2/6-311+G(3df,2p) converge to a 60 cm^{-1} splitting of the v_2 and v_9 bands as compared to 42 cm^{-1} found experimentally. The difference is attributed to the strong interactions of the CH stretch with the HCH bending overtones and combinations.

(ii) Double resonance IRLAPS (Infrared Laser Assisted Photodissociation Spectroscopy) experiments on both C-12 and C-13 methanol have have found that the torsional barrier doubles when the O-H stretch is excited up to $6v_1$. *Ab initio* calculations show that the torsional barrier increases for OH distances both longer and shorter than the equilibrium bond length. This result can be explained in terms of partial double bond character on the CO bond.

The Potential Energy Surfaces of HOCl and HOBr: Vibrational Energy Levels and UV-Vis Absorption Cross Sections

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Accurate global potential energy surfaces have been calculated for the electronic ground states of HOCl and HOBr, as well as the first four excited electronic states of HOBr. Vibrational energy levels up to the lowest dissociation channel, e.g., HOCl $\rightarrow$ OH + Cl, have been calculated[1] for the ground states of both species, including the the HClO and HBrO isomers. In the case of HOBr, UV-Vis absorption cross sections have been calculated that include the effects of spin-orbit coupling. In addition to the weak feature near 457 nm due to the a^3A'' state, SO coupling results in a relatively strong $b^3A' \leftarrow X^1A'$ transition that contributes significantly to the peak near 350 nm that was previously assigned experimentally to the $A^1A'' \leftarrow X^1A'$ transition.

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NONADIABATIC EFFECTS ON THE He + NO_2 COLLISIONAL ENERGY TRANSFER

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We present the results of an accurate quantum scattering study of collisional energy transfer in the collinear He + NO_2 system, considering energies up to 45 kcal/mol above the minimum of the NO_2 X^2A_1 ground state potential. We have used a coupled channel formalism, 329 NO_2 nonadiabatic states and levels, up to 40 kcal/mol, due to the X^2A_1/A^2B_2 conical intersection, and a Lennard-Jones 6-12 intermolecular potential.

The cross section distributions at 300 and 1000 K, obtained by Boltzmann averaging over the translational energies, show considerable mode-specific behavior, with overall envelopes nearly exponential. The elastic cross sections are always dominant and the other peaks follow the NO_2 X^2A_1 bending-asymmetric stretching progressions: the largest inelastic cross sections are due to the decrease of one X^2A_1 bending quantum, the bending mode is most active, and the symmetric stretching is inactive.

The Boltzmann-averaged first moments show that the NO_2 X^2A_1/A^2B_2 nonadiabatic mixing and the X^2A_1 bending character of the nonadiabatic states are very important, since the moments for the electronically mixed states, which also correspond to X^2A_1 high bending quanta, are much larger than for other states. Because the A^2B_2 diabatic vibrational states have negligible moments, the nonadiabatic mixings between X^2A_1 high bending states and their A^2B_2 partners are crucial for the collisional energy transfer, which increases up to six times with respect to the diabatic results. Finally, by averaging the state-selected moments over an exponential gap distribution of NO_2 internal energies, we have obtained microcanonical moments which are in good agreement with the experimental results by Hartland et al.

A theoretical study of the $O(^1D)$ + HCl reaction.

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In recent years the electronically excited oxigen atom hydrogen-halide molecule reactions have been extensively investigated both experimentally and theoretically. However, only very recently a potential energy surface based on *ab initio* values has become available for the prototype system of this family $O(^1D)$ + HCl [1]. Due to the fairly heavy mass of the intervening atoms and to the large exoergicity of the reactive process, calculations are difficult to perform using time independent approaches. For this reason a time-dependent quantum approach (TDQM)[2] has been used. TDQM techniques make use of time as a continuity variable to integrate the corresponding time dependent Schrödinger equation. The success of TDQM emanates from its simplicity, both in the implementation phase and in the result interpretation phase. Moreover the TDQM technique used for our calculations operates on real quantities only [3]. In time dependent approaches one prepares the initial wave function for a specified set of initial conditions and then lets it evolve in time until the effect of the hamiltonian application has been fully produced.

In our laboratory we have calculated reaction probabilities for the system $O(^1D)$ + $HCl(v,j) \rightarrow OH(v',j') + Cl$ for energy values ranging from 0.3 to 0.9 eV and far the first and the second vibrational state. The total angular momentum J was set equal to zero. In the investigated interval of energy, the reactive probability calculated increases from 0 to 0.3838 eV and shows a rich resonance structure. Such a rich structure is not surprising due to the existence of a double well stabilizing intermediate HOCl and HClO complexes.

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Gas phase electronic spectra of cold, polycyclic aromatic cations : new clues for radiationless transitions in large molecules.

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We have developed an experimental method devoted to the spectroscopy of cold and isolated Polycyclic Aromatic Hydrocarbons (PAHs) cations in the gas phase[1,2]. The goal was to obtain electronic spectra of these species in conditions close to those of the InterStellar Medium (ISM). Indeed, the family of the PAH molecules is expected to be an important constituent of the ISM since it should contain up to 15% of the cosmic carbon[3] (derived from IR observations). But no clear identification has been achieved yet, and the visible to near infrared absorption spectra of these molecules when ionized may provide a powerful tool to detect them.

To obtain these spectra, we use a trick consisting in monitoring the photodissociation spectra of the related $PAH^+-Ar_{1,2}$ Van der Waals complexes. One can form cold and isolated PAH^+-Ar_n complexes by combining molecular beam and resonant 2-photon ionisation (R2P2CI). Because the binding energy of Ar in these Van Der Waals clusters is small (of the order of 500 cm^{-1}), the complex is easily fragmented by exciting the molecule above this dissociation threshold (this process occurs on a subnanosecond time-scale). Thus resonant absorption of a third laser photon can induce the ejection of the rare gas atom, and the appearance of the fragment PAH^+ reflects the spectroscopy of the parent[1,2,6].
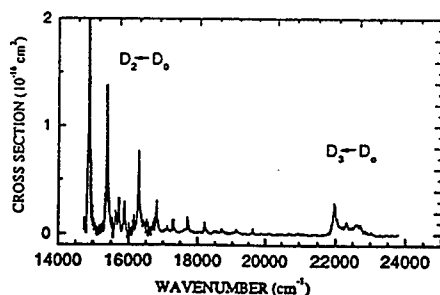

Figure : Visible absorption spectrum of Naphtalene[+]-Ar [4] (cross section scale on the left hand side). The origin of the D_2 (14867 cm^{-1}) has been truncated (60%) for convenience. Note the difference in the FWMH of the two electronic transitions : 20 cm^{-1} for D_2 state, 90 cm^{-1} for D_3 state (21956 cm^{-1}).

The result obtained for several cations, Phenanthrene[+][1], Naphtalene[+][4] (see figure), Fluorene[+][5], Pyrene[+][5], show that relaxation of the excited electronic state is dominated by radiationless transitions occuring on a timescale ranging from 400fs (for the D_2 state) to 40fs (for the higher D_n states). This process is the starting point for the intra- and inter-molecular energy transfer leading to the release of the Ar, with a quantum efficiency of unity. For this reason these photodissociation spectra are equivalent to absorption spectra.

At present, calculations are in progress[7] to analyse the electronic structure of these cations and draw conclusions about the intramolecular dynamics of these species. The relevance to the detection of polyatomic cations in the ISM via their electronic spectra is investigated as well.

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Molecular Alignment in Supersonic Seeded Beam Expansions: Experiments and a Quantum Mechanical View

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In 1994 we presented the first evidence of the strong dependence on final speed v of rotational alignment induced by collisions of molecules emerging from supersonic expansions [1] by measuring the variation of paramagnetism of O_2 in continuous seeded beams of molecular oxygen. Subsequently, measurements of anisotropy effects on collision cross sections for the O_2-Xe, N_2-Xe, O_2-Kr and O_2-O_2 systems, confirmed the correlation between molecular alignment and molecular velocity.

After our initial reports on this subject, related works using laser probing of N_2^+ drifted in He [2] and of CO in a He seeded supersonic pulsed beam [3] appeared, bringing further evidence of the dramatic dependence of molecular alignment on the final velocity.

Several attempts have been performed in the past to model the mechanism of collisional alignment. The success of original mechanism of Gorter [4] along the years is based on its simple geometrical appeal, but such an approach is clearly inadequate to describe effects such as the velocity dependence of the alignment, which selectively depend on elastic and inelastic collisions in defined range of impact parameter.

For a meaningful analysis of collisional alignment effects, close attention must be paid to the quantum state-to-state differential cross sections (DCS), which have been calculated in this work for the prototype system O_2-He. The DCS exhibit propensities which appear relevant to reveal nature and selective role of elastic and inelastic scattering events, which takes part in each mechanism, yielding molecular alignment and cooling. The present analysis suggests that the dynamics of such phenomena crucially depends on the involved initial and final rotational state and on the range of energy and of orbital angular momentum mainly probed by the collisions. As a consequence, molecules following defined roots are scattered into specific angular cones. Moreover rotational-to-translational energy transfer has been recognized as the main acceleration mechanism for low rotational states, as pertinent for the O_2 case.

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The full dimensional quantum and quasi-classical trajectory calculations for the $H_2 + OH \leftrightarrow H_2O + H$

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The $H_2 + OH \leftrightarrow H_2O + H$ reaction has became the benchmark for four-atom reactive scattering calculations in recent years. Recently a new potential energy surface for this reaction has been developed by Ochoa and Clary. We use this surface to carry out the full 6D time-independent quantum scattering calculations based on the arrangement channel hyperspherical coordinate method. Also quasi-classical trajectory calculations are performed. The latest results, including a comparison with the available experimental data, will be presented at the conference.

The spectroscopy and IVR dynamics of HOCl in the v_{OH}=6 region, probed by infrared-visible double resonance overtone excitation.

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Abstract

We use infrared-visible double resonance overtone excitation to prepare HOCl molecules in single, well-characterized rotational levels of high OH stretching states just above the HOCl $\rightarrow$ HO + Cl dissociation threshold on the ground potential energy surface. We obtain double resonance spectra using laser induced fluorescence (LIF) of the OH dissociation products as the detection mean. We show here the results obtained in the $6v_1$ region of $HO^{35}Cl$ where we have studied states with J ranging from 4 to 25, K_a from 0 to 5 and energy up to 300 cm^{-1} above the dissociation threshold. The energy of the O-Cl bond is determined to be 19290.3 cm^{-1} by observing which states of the parent molecule lie above or below the dissociation threshold. In the spectra for K_a=0-3 states, the zeroth-order (v_{OH}, v_{ϑ}, v_{OCl}) = (6,0,0) level is split by mixing with a nearby dark state. As the two states have very different A rotational constants, their separation increases with K_a, but the effects of the mixing remain observable in the spectrum up to K_a=3. Analysis of the rotational constants and isotope shift allows us to identify the perturbing state as (4,4,2).

FEMTODYNAMICS OF DOUBLE PROTON TRANSFER IN 7-AZAINDOLE DIMER

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The proton transfer induced tautomerization has recently received a great deal of attention. The development of new femtospectroscopy techniques has made possible the experimental study of this reaction. So Zewail and co-workers and Folmer and co-workers have done recent experiments on 7-azaindole dimer using these techniques. The study of the dynamics of the tautomerization process on 7-azaindole dimer will give us an understanding of a similar process in DNA base pairs which could explain some mutations in different biological systems.

We have been working on the proton transfer induced tautomerization of 7-azaindole dimer. The aim of this work is to explain the mechanism of the double proton transfer in this molecule and to predict the timescale of the reaction.

In order to achieve this, we used the quantum tunnelling in a dissipative environment method proposed by M. Hron and M. Razaby. This method considers that the system is composed of a central particle (the H atom in our system) moving in a potential field that is coupled to a number of noninteracting harmonic oscillators forming the heat bath.

This method will allow us to calculate the proton transfer time. Its value depends on the type of coupling between the particle's motion and the heat bath. A estimation of the value of the coupling term was obtained from ab-initio data. In this conference we are going to present the results of this theoretical study. Times for double proton transfer will be compared with the experimental results mentioned above.

Spin-orbit branching in Cl (^{2}P) atoms produced by ultraviolet photodissociation of HCl and DCl

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Hydrogen cloride is the simplest amongst hydrogen halide molecules for which significant progress has been made to investigate the photodissociation dynamics following excitation in the UV region and quantitative agreement between experimental and theoretical approaches is now achievable.

The first UV absorption band of HCl arises predominantly from transition from the ground $X^1\Sigma^+$ state to the repulsive $A^1\Pi_1$ state and an adiabatic dissociation on this PES would only produce H in the ground ^{2}S state and Cl in its ground spin-orbit state ^{2}P3/2. Theoretical calculations have demonstrated that non adiabatic transitions, governed by spin-orbit coupling and occuring at large internuclear distance, are responsible for redistribution of the photofragment flux among the two thermodynamically accessible channels [H(^{2}S) + Cl(^2P_j)]. A strong H/D isotope effect on the branching fractions for Cl(^{2}P$_{3/2}$) and Cl*(^{2}P$_{1/2}$ has also been predicted and is related to the smaller nonadiabatic transition probability for the system with the heavier reduced mass.

On the line of previous work on HI and HBr [1], we have investigated the photodissociation dynamics of jet-cooled HCl molecules following excitation at 5 wavelengths in the range 201-210 nm. Ground state hydrogen photofragments H(^{2}S) have been detected using the H Rydberg atom time-of-flight technique to obtain the relative yields of the available product channels. The product branching fractions will be presented and compared with recent theoretical calculations and experimental measurements [2, 3, 4].

The two spin-orbit components of Cl fragments formed by photolysis of HCl at 205.5 nm have also been monitored using (2+1) REMPI transitions for Cl and Cl* around 235 nm. By comparing the branching fractions obtained via the Rydberg atom technique with the relative REMPI signals, it has been possible to calibrate for the different 2-photon line strengths for excitations.

We are presently extending experimental measurements of branching fractions for DCl (presently only available at 157 and 193 nm) to longer wavelength in the range 200-220 nm, using REMPI detection of Cl atoms and the calibration factor for ionization probabilities previously determined. Preliminary results are in quantitative agreement with theoretical calculations.

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State-resolved intra-and unimolecular dynamics in highly excited *trans*-HONO by double resonance overtone photofragment spectroscopy

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The intra- and unimolecular dynamics of *trans*-HONO after IR-VIS OH-overtone excitation ($5v_1$, $6v_1$ and $7v_1$) has been investigated using (time resolved) double resonance overtone photofragment spectroscopy. The obtained double resonance spectra contained rich information about molecular constants, intramolecular dynamics, and lifetimes of the highly excited transient molecules. From the J and K dependence of the overtone spectra the dissociation threshold could be determined with high precision ($E_0=16786.7\pm0.6$ cm^{-1}). In addition, rotational constants, band origins, perturbations, and product state distributions have been determined. Time resolved product formation in single OH-states, directly measured dissociation rates, linewidths of single resonances of the parent molecules and the product state distributions have been compared with predictions from statistical theories like SACM and PST. The molecule excited in individual overtones showed different intramolecular dynamics, depending upon the number of quanta in v_1. The number and the strength of intramolecular (low-order) couplings to dark background states was found to increase with increasing OH excitation. However, even in the case of $7v_1$ the rotational structure was still found to be regular which suggests that the zeroth-order OH-stretching mode is only weakly coupled to other vibrations of the molecule. Interestingly, the intramolecular dynamics competes in a subtle way with unimolecular dissociation, a process with is possible only after energy flow from the originally excited mode(s) to the breaking bond. A full analysis of the different intramolecular couplings, mechanisms of intramolecular dynamics, and excited state lifetimes in different overtones of v_1 of *trans*-HONO above the dissociation threshold will be presented at the conference.

Spin orbit selectivity of elementary reactions at very low temperature

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Abstract

The open shell nature of the reactants is known for a long time to have important effects in chemical reaction of astrophysical interest. For example, OH and CH interstellar maser emission is due to specific Λ doublet preferences of OH or CH producing reactions. Furthermore, recent experimental[1] and theoretical studies[2] in the last ten years demonstrated that reactions between neutral species, involving radicals and open-shell atoms, can exhibit large rate coefficients even at low temperatures (T < 300 K). Some of these exothermic neutral-neutral reactions recently received more attention in atmospheric and especially interstellar chemistry because they are supposed to profoundly influence the evolution of molecular abundances in interstellar dense clouds. In this work[3] we treat the general case of an atom in a ^2P or ^3P electronic state reacting with a linear molecule in a $^2\Pi$, $^2\Sigma$ or $^3\Sigma$ electronic state. We demonstrate that the spin orbit selectivity of the rate constant at very low temperatures (T < 10 K) is associated with the different contributions to the long range intermolecular potential calculated in the spin orbit basis set of the reactants. We eventually give examples of application to a few reactions of astrophysical interest.

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Collisional effects on angular momentum orientation
in acetylene X $^1\Sigma$ (v_2'' = 1,J'')

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We will present results of experiments on collisions with oriented and aligned angular momentum of acetylene molecules. Stimulated Raman pumping is used to selectively prepare single rotational states in the carbon stretch vibration of acetylene. With circularly polarised pump light and the proper choice of transition strongly oriented molecules with $A_0^{(1)}$ up to 0.8 can be prepared. Similarly, using linearly polarised pump radiation the preparation of strongly aligned molecules with $A_0^{(2)}$ up to -0.7 is possible [1,2]. Due to the influence of the ac Stark effect a slightly higher orientation can be achieved [3] than calculated from a low-field theory [4]. Laser-induced UV fluorescence is used to monitore the population and the angular momentum orientation in specific rotational states of $v_2 = 1$.

For rotationally elastic collisions the decay of the originally prepared orientation has been measured for J'' = 3 to 13. The decay rate slowly decreases with increasing J'', and assumes average values of about (8 ± 2) μs^{-1} Torr^{-1}. This rate is about a factor of 3 slower than the decay of the population in the states, which amounts to about $k_{tot} = (25 \pm 2)$ μs^{-1} Torr^{-1}, and it is half as fast as the gas kinetic collision rate of 16.6 μs^{-1} Torr^{-1} at T = 300 K.

In rotationally inelastic collisions a significant fraction of the initially prepared orientation is retained. For $\Delta J = 2$ transitions $A_0^{(1)}$ drops to about 50% its original value, for $\Delta J = 4$ and 6 a decrease of the orientation to about 38% and 30%, respectively, of the prepared orientation is observed. This shows that in pure acetylene a change of the rotational angular momentum is predominantly induced by planar collisions. A model calculation for m_J - changing collisions is presented which reconciles these data with earlier ones obtained from alignment measurements [2].

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The correlation approach to studies of chemical processes (by an example of the $F + H_2$ system)

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The dynamics of any elementary chemical process is entirely determined by the topography of the corresponding potential energy surface (PES), and the construction of adequate PESs as well as the diagnostics of PESs is therefore one of the main important tasks of the theory of atomic and molecular collisions. This report is devoted to the correlation analysis, one of the simplest ways to reveal the mutual dependence of the PES characteristics and the scattering processes governed by those PESs. We have applied the correlation approach, within the quasiclassical trajectory framework, to the reaction

$$F + H_2(D_2)[v_i = j_i = 0] \rightarrow H(D) + HF(DF)[v_f, j_f]$$
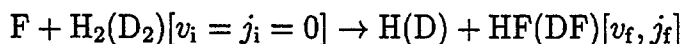
which has attracted much attention in the last 15 years as a model example for developing experimental techniques (primarily based on crossed molecular beams) with superhigh resolution and working out methods of fitting PESs for multi-electron systems.

We have exploited the five-parameter family of semiempirical LEPS-type PESs proposed in [1], this family including the Muckerman M5 surface and the Takayanagi–Sato TS surface. Over collections of 91 collinear PESs and 296 non-collinear PESs, we have calculated the correlation coefficients between parameters p_j of quasiclassical trajectories and parameters P_k characterizing the topography of the surface, as well as the "second order" correlation $\{p_i \longleftrightarrow p_j\} \longleftrightarrow P_k$ coefficients. On each surface, the statistics of 2500 reactive trajectories with initial conditions chosen randomly was accumulated. The set of trajectory parameters p_j contained the collision energy E_{col} (which varied in the range 70 meV $\leq E_{col} \leq$ 200 meV), the impact parameter b, the scattering angle θ, the product quantum numbers v_f and j_f, and some other parameters. The surface parameters P_k pertained primarily to the angular dependence $E_0(\gamma)$ of the reaction barrier height, γ being the attack angle, i.e., the Jacobi angle between the target axis and the vector connecting the fluorine nucleus and the target center-of-mass. The set of parameters P_k included the collinear barrier $E_0(0)$, the angle γ_{min} where the barrier height attains the minimum [$\gamma_{min} = 0$ for collinear surfaces], the minimal barrier $E_0(\gamma_{min})$ [for non-collinear surfaces], the Jacobi coordinates $R_*(0)$, $r_*(0)$ and $R_*(\gamma_{min})$, $r_*(\gamma_{min})$ of the barrier top, the "width" parameter w of the dependence $E_0(\gamma)$, and some other parameters.

An analysis of the sets of the correlation coefficients enables one to obtain quantitative data about the effect of the surface parameters on the measurable process characteristics and, consequently, to change the PES topography purposefully to attain the most adequate description of the experimental data.

For instance, the coefficients of the correlations $v_f \longleftrightarrow P_k$ imply that broadening the dependence $E_0(\gamma)$ results in the relative enhancement of the population of $HF(v_f = 3)$ and $DF(v_f = 4)$ molecules—the highest accessible vibrational states of the products. The coefficients of the correlations $\{E_{col} \longleftrightarrow \theta\} \longleftrightarrow P_k$ show that the larger $E_0(\gamma_{min})$, $r_*(\gamma_{min})$, or $[R_*(\gamma_{min})]^{-1}$, the more pronounced is the selective growth (observed experimentally) of forward scattering of the $HF(v_f = 3)$ and $DF(v_f = 4)$ products as the collision energy increases.

[1] V. M. Azriel, L. Yu. Rusin, M. B. Sevryuk, J. P. Toennies, Chem. Phys. **232** (1998) 307, Russian J. Phys. Chem. **72** (1998) 1207.

STUDY OF OVERTONE STATES IN HCCH AND H₂O BY LASER INDUCED FLUORESCENCE

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The method of laser induced fluorescence (LIF) has been applied to study highly excited vibrational overtones of acetylene and water in the ground electronic state in the near infrared range. This method offers some advantages compared to conventional one-photon absorption techniques. It gives us an access to vibrational states that cannot be populated by one-photon transitions from the ground state and it permits to study the processes of rovibrational energy redistribution by collisions.
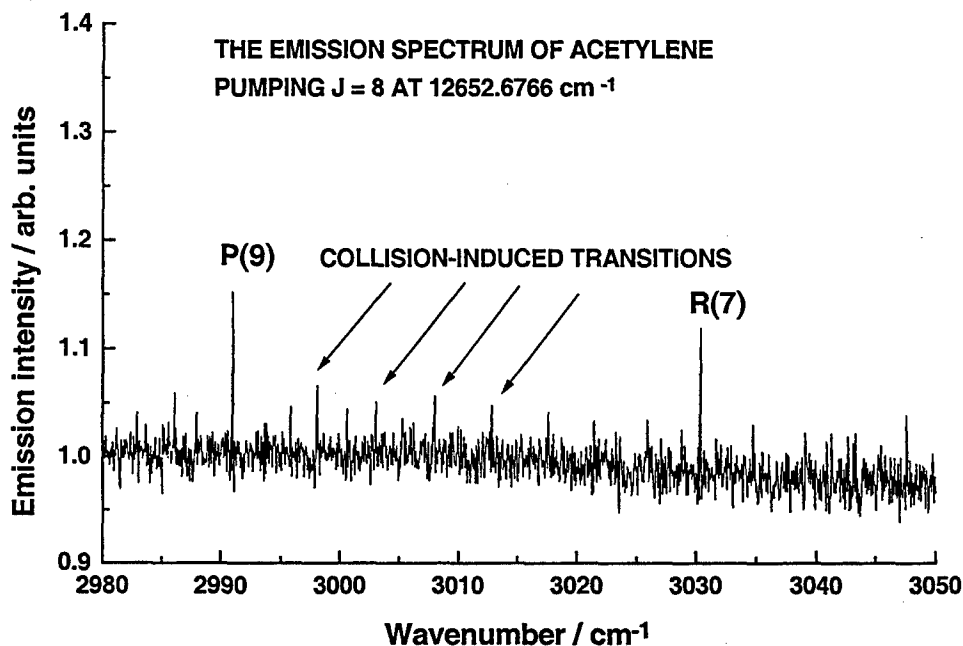
The cell containing the sample at the room temperature has been placed inside a Ti:Sapphire ring laser cavity. The fluorescence signal has been collected by a parabolic mirror and directed into a high resolution FTIR-spectrometer. The dispersed fluoresence has been detected in the 2800 - 4000 cm^{-1} range. By pumping different single vibration-rotation lines in the near infrared range we have measured the dispersed fluorescence from the third CH-stretching overtone in acetylene and from the second OH-stretching overtone of water. Many collision-induced rovibrational transitions from the upper state have been observed per one pumping line for both molecules.

Photoelectron and photofragment velocity imaging following the excitation of CH3I to the A-Band using fs, ps and ns laser pulses

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Abstract

Multiphoton processes following the excitation of methyl iodide to the A-band continuum are studied using a pulsed laser beam of 5 eV photons with pulse duration of 15 ns, 5 ps and 500 fs. Velocity map images are obtained for the resulting photoelectron, I^+ and CH_3^+ fragments. Both one-photon dissociation and multi-step ionization are observed, the latter process becoming dominant at the shorter pulse duration. The PhotoElectron Spectra (PES) obtained from velocity map imaging, which provides uniform transmittance for all electron kinetic energies, show that two-photon excitation of CH_3I mediated by the dissociative A-band leads to the production of CH_3I^+ in a number of overtone progressions with non-Franck-Condon intensity distributions. The vibrational distributions obtained are compared with ZEro Kinetic Energy (ZEKE) and magnetic bottle PES measurements under similar conditions. Velocity images of the I^+ and CH_3^+ show a marked anisotropy whose angular dependence on the scattering angle varies strongly with the laser pulse duration. At progressively shorter pulse durations, multiphoton ionization / fragmentation of CH_3I^+ dominates the observed signal.

MOLECULAR ALIGNMENT EFFECTS ON THE DYNAMICS OF THE REACTIONS H + HX → H$_2$ + X (X=Cl, Br, I): A QCT THEORETICAL STUDY

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The experimental and theoretical efforts devoted to the understanding of the gas phase reaction dynamics have been mainly focused on scalar properties, such as the total cross section and energy partitioning in products. However, a complete understanding of the reaction dynamics is only possible after accounting for both scalar and vector properties together. In this work, the following set of reactions has been considered, using the quasiclassical trajectory (QCT) method:

   H + HX → H$_2$ + X (X=Cl, Br, I)   (ΔE= -0.13, -0.81 and -1.55 eV respectively)
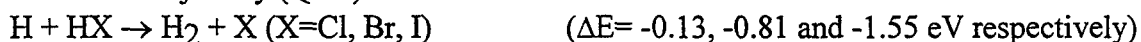
The influence of considering perpendicular (perp.), parallel (par.), and random (null) initial **k-j** alignment on the dynamics of these reactions (exoergic triatomic reactions with L-L-H kinematics and collinear saddle point) have been studied. Threshold energy for parallel alignment is always higher than the ones for perpendicular and null alignments. However, although s(par.) is lower than s(perp.) and s(null) at low and moderate relative translational energy (E$_T$) values, as E$_T$ increases s(par.) becomes larger than s(perp.) and s(null). The same also applies when the dependence of s on the HX vibrational or rotational levels is considered. These results and others concerning scalar properties may be justified on the basis of the saddle point properties and geometrical implications of the alignments. The dependence of the differential cross sections for the angles k-k', k-j', k'-j' and l'-j' on the initial conditions (E$_T$, v, j, alignment) can be rationalized considering the increase of "effective molecular size" produced when the HX molecule is vibrationally excited, and the fact that it is easier for an H atom to approach the HX molecule with a situation near to insertion for parallel alignment (side-on attack), than for the perpendicular one (end-on attack). The vector correlations obtained are not a trivial result coming from kinematics, being particularly remarkable the role played by the rotational angular momentum of the HX molecule on them. For both scalar and vector properties, the results obtained for perpendicular alignment are in general closer to the ones for null alignment than the results arising from parallel alignment.

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AB INITIO STUDY OF THE GROUND AND FIRST EXCITED PES's
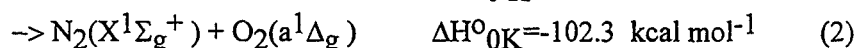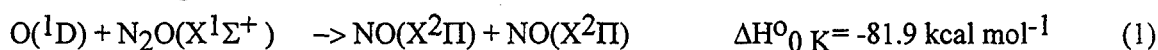## OF THE $O(^1D) + N_2O \rightarrow 2\ NO,\ N_2 + O_2(a^1\Delta_g)$ REACTIONS

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C/ Jordi Girona, 18-26. 08034 Barcelona (Spain)

The reaction of N_2O molecules with $O(^1D)$ atoms, which arise primarily from the photodissociation of ozone in the 200-300 nm wavelength region, is considered to be the main source of the stratospheric NO. This radical plays a relevant role in the natural degradation of ozone and the $O(^1D) + N_2O$ reaction presents the following reaction channels:

$$O(^1D) + N_2O(X^1\Sigma^+) \rightarrow NO(X^2\Pi) + NO(X^2\Pi) \qquad \Delta H^o_{0\ K} = -81.9\ kcal\ mol^{-1} \qquad (1)$$
$$\rightarrow N_2(X^1\Sigma_g^+) + O_2(a^1\Delta_g) \qquad \Delta H^o_{0K} = -102.3\ kcal\ mol^{-1} \qquad (2)$$

If one assumes the C_s symmetry for the system, there are 2 PES's of $^1A'$ symmetry and 2 of $^1A''$ symmetry correlating with NO + NO, and only one of each type correlating with $N_2 + O_2$ (a $^1\Delta_g$). Therefore, there is one $^1A'$ and one $^1A''$ PES connecting reactives, $O(^1D) + N_2O$, with both kinds of products. We have studied theoretically the ground ($1^1A'$) and first excited ($1^1A''$) PES's by means of the CASSCF and CASPT2 *ab initio* methods employing the 6-311G(2d) basis set and a (18, 14) maximum active space. For the $1^1A'$ PES and channel (1), the $O(^1D)$ atom attacks the terminal N atom of the NNO molecule and evolves through a TS to a symmetric minimum in which there is a NN double bond. The elongation of the NN distance leads to the exit zone with three stationary points representing two interacting NO molecules, and finally to products. For channel (2), the attack of the $O(^1D)$ atom to the other end of the NNO molecule leads to a very different behaviour to that observed in channel (1), since the system passes through two minima and two TS's with little distorsion of the NNO molecule, i.e., it is still the entrance zone. From the TS presenting the shorter OO distance the energy goes down abruptly bringing about the products. Generally speaking, for the $1^1A''$ PES the tendencies observed are the same as those for the $1^1A'$ surface; the barriers show a strong decrease on moving from the CASSCF to the CASPT2 level, though this time the TS's energy is above the energy of reactives. The present calculations show that the ground PES possibly presents no barrier to products. Additional calculations on the remaining PES's ($2^1A'$ and $2^1A''$, only correlating to 2 NO), performed with the smaller (14,12) active space, indicate that they are too high in energy to be meaningful for the reactivity of the system.

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REACTION OF H WITH HIGHLY VIBRATIONALLY EXCITED WATER

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The dynamics of the collisions of H atoms with vibrationally excited H_2O were studied using quasiclassical reactive and quantum mechanical nonreactive scattering calculations. These calculations were performed with the recently developed OC potential surface of Ochoa and Clary, and we also present results obtained earlier using the somewhat older I5 surface of Isaacson. Both surfaces were derived by fitting ab initio calculations, and the saddle point properties are quite similar. The quasiclassical trajectory results for the OC surface show that although this endoergic reaction is activated for reaction with water in its vibrational ground state, and the (01)⁻ state (one quantum of OH stretch), excitation to the (02)⁻ state is sufficient to switch the potential to be attractive at long range, so that the cross section diverges at low translational energy. Similar behavior, but with larger cross sections, are seen for the (03)⁻ and (04)⁻ states, and as a result, the reactive rate coefficient is very large for these states, being a significant fraction of the gas kinetic rate coefficient. This behavior is qualitatively different from what is obtained using the I5 surface which shows activated behavior even for excitation as high as (04)⁻. To verify the accuracy of the OC surface, we have performed high quality ab initio calculations for the H + H_2O system for geometries in the reagent region that correspond to high OH stretch excitation, and we find that the OC surface is qualitatively correct, but with too long a range in its attractive tail. However, the switch from activated to activationless behavior should still occur at the (02)⁻ state, so the rate coefficients for reaction starting in states (02)⁻ and higher should still be large. Our quantum calculations of the vibrationally inelastic rate coefficients on the OC surface give values for the total inelastic rate coefficients starting in (02)⁻, (03)⁻ and (04)⁻ that are comparable in magnitude to the rate coefficients for reaction out of the same levels. This suggests that in the recent measurements by Smith and coworkers of the rate coefficients for total loss from (04)⁻ reaction and vibrational energy transfer are of comparable importance.

IR-Laser induced Processes in Low Temperature $C_2H_2^+$ + H_2 collisions

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Laser excitation in a low temperature rf 22-Pole ion trap is used to stimulate the reaction $C_2H_2^+$ + H_2 → $C_2H_3^+$ + H. The excitation frequency is in the range of the asymmetric C-H stretch vibration (3.1 μm). It is produced by nonlinear difference frequency generation of a Nd:YAG laser and a dye laser. Mass selective single ion counting detection of the $C_2H_3^+$ products serves as a very sensitive probe of the IR-excitation of the $C_2H_2^+$ reactants. Scanning the IR-laser an action spectrum of $C_2H_2^+$ is obtained. While for conventional IR spectroscopy methods number densities of $>10^8$ cm^{-3} and optical path lengths extending the meter range are necessary, the spectrum shown is taken with only several thousand ions stored at each wavelength. The universality of this new method has been demonstrated earlier in our group for the charge transfer reaction N_2^+ + Ar + hν → Ar^+ + N_2 [Int. J. Mass Spectrometry and Ion Processes, 185-187, 589-602, (1999)].

Besides the very interesting aspects concerning background free, mass selective, high resolution spectroscopy of molecular ions the elementary reaction steps of the more complex reaction scheme can be followed in our experiment in detail as a function of various reaction parameters. Most interestingly the use of laser excitation allows for the preparation of rotationally and fine-structure selected reactants. As a preliminary result the rate coefficient for $C_2H_2^+(v_3=1)$+H_2 → $C_2H_3^+$+H shows a strong rotational dependence. Further experiments, e.g. involving the asymmetric bending mode (v_5), are in progress. In future studies this new tool will be applied to other interesting quasi-thermoneutral reactions.

Local density effects in the energy relaxation of vibrationally highly excited molecules from the gas to the compressed liquid phase.

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We report on systematic investigations of the density and temperature dependence of vibrational energy transfer from highly excited small (CS_2) and large (azulene) molecules to a bath, respectively. Energy relaxation rates are compared with solvatochromic shifts Δv of electronic absorption bands of these molecules under identical conditions. Employing supercritical fluids, such as xenon, CO_2, and ethane, at pressures between 0.03 and 4000 bar and temperatures between 298 and 640 K, measurements covering the complete gas-liquid transition were performed.

Activated azulene with an energy of ~20000 cm^{-1} was generated by laser excitation into the S_1- and internal conversion to the S_0^*-ground state. The subsequent loss of vibrational energy was monitored by following the transient absorption at the red wing of the $S_3 \leftarrow S_0$ absorption band near 290 nm. Transient signals were converted into energy-time profiles using hot band absorption coefficients from shock wave experiments for calibration and accounting for solvent-shifts of the spectra. Under all conditions, the energy decays of azulene were found to be exponential with phenomenological deactivation rate constants k_c. A comparison of k_c and spectral shifts Δv showed quite similar density dependencies: the low pressure linear increase of both quantities at $\rho_r = \rho/\rho_c \approx 0.1$ (ρ_c is the critical density of the solvent) starts to level off, before it finally becomes stronger again. These observations suggest that both quantities are determined by the same local bath gas density around the azulene molecule.

Vibrationally highly excited CS_2 was generated with excess energies of 32000 cm^{-1}. The energy decays were monitored at 266 nm. Hot CS_2 UV-spectra from shock wave studies were used to convert absorption signals into energy decay curves. In contrast to azulene the energy decays of CS_2 are highly non-exponential. However, for a given collider the shapes of these energy decay curves look the same in the gas phase and in the liquid, if the time axes is scaled properly. This allows for extracting mean deactivation rate constants which show similar density dependencies as observed for azulene.

The data are analyzed employing isolated binary collision (IBC) models and perturbation theory. Within the IBC approach $k_c(\rho)$ can be modeled, if the collision frequency Z is related to the radial distribution function $g(r)$ of an attractive hard-sphere (AHS) particle in a Lennard-Jones fluid. For the system azulene in ethane, average energies $\langle \Delta E \rangle$ transferred per collision are shown to be temperature independent between 298 and 640 K and pressure independent between 0.03 and 4000 bar.

The same agreement with the experimental data can be obtained within the weak coupling approach when $k_c(\rho)$ is related to the spectral density of the fluctuating force exerted by a Lennard-Jones solvent to a breathing Lennard-Jones sphere.

Hot Atom Reaction Yields for Mu* + H_2 and T* + H_2 Calculated from Atom-Molecule Cross Sections on the LSTH Surface.

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and
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Arguably, still the only truly chemically accurate ($\sim 0.1 kcal/mol$) PESs known are the LSTH, DMBE and BKMP potentials for the H_3 system. Accordingly, there has been an impressive array of experimental results spanning the past decades (and continuing) for both thermal rate constants and inelastic and reactive scattering, up to $\sim$ 2 eV energies, for the isotopic variants of the H* + H_2 → H*H + H reaction, including the thermal reaction rates of the muonium atom, most of which give excellent if not exemplary agreement with theory. In the arena of rovibrational excitation the BKMP potential seems to give the best results, particularly when effects due to geometric phase are included, but the earlier LSTH surface and particularly QCT calculations on this surface towards higher collision energies, also give an excellent account of much of the data. In order to provide a further assessment of the " global" accuracy of this surface for H_3, hot atom reaction yields, which are determined from energy transfer in collision processes over a wide energy range, have been calculated for the Mu* + H_2 and T* + H_2 systems. The isotopic comparison of muonium (Mu= μ^+e^-), the lightest isotope of hydrogen ($m_{Mu}/m_H \approx 1/9$), with the heaviest H-atom isotope, tritium, is a novel approach in testing the global accuracy of the H_3 surface. These reaction yields have been calculated using a formalism developed for (μ^+) charge exchange, with input cross sections for elastic, inelastic (rovibrational excitation) and reactive collisions determined from Quasi Classical Trajectories on the LSTH surface, in the center-of-mass energy range 0.5 to 11 eV. The rate of energy loss of the hot atom (Mu* or T*) due to elastic and inelastic collisions with the moderator (H_2) drastically affects the hot atom reaction yield and hence the assesment of the surface. In particular, the forwardness of the angular differential cross section for the *elastic* process plays a crucial role in determining the stopping power for hot atoms. Good (20%) agreement is obtained in the *absolute* yields for both Mu* + H_2 and T* + H_2, for the *first* time from *microscopic* cross sections, demonstrating that the LSTH surface remains suprisingly accurate over a wide range of energy and isotopic mass (factor of 25).

Reaction Dynamics of Ground State and Electronically Excited Neutral Transition Metal Atoms with Alkanes

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The reactions of transition metal atoms (M) with saturated hydrocarbons such as methane, ethane, and cyclopropane are believed to be initiated by direct C-H bond insertion, without initial complex formation. Although there is considerable interest in better understanding the electronic and dynamic factors controlling the heights of potential energy barriers for such reactions, very few direct experimental studies on such systems have been carried out. Room-temperature flow cell studies indicate that first and second row ground state transition metal atoms are generally unreactive with alkanes at low collision energies due to the presence of substantial potential energy barriers for C-H or C-C insertion.

Using the technique of crossed molecular beams, we are studying the reaction dynamics of ground state and electronically excited transition metal atoms with alkanes. Using the seeding technique, we can study reactions having substantial potential energy barriers and, by studying the reactivity as a function of collision energy, determine barrier heights for direct comparison with theoretical predictions. Using "universal" mass detection of the chemical products and the nonreactively scattered metal atoms, we are able to gain insight into all competing channels.

To date, we have studied the nonreactive and reactive collisions between second-row transition metal atoms (Y, Zr, Nb, Mo) and several simple alkanes. In the case of Y, Zr, and Nb, insertion into the C-H bond of C_2H_6 is followed by H_2 elimination, forming MC_2H_4. Ground state Mo (^7S) atoms, on the other hand, are found to be unreactive even up to collision energies of ~ 30 kcal/mole, implying the existence of a large potential energy barrier for reaction. However, the metastable electronically excited Mo (^5S) state, prepared by optical pumping upstream of the collision zone, is found to react efficiently with methane and ethane at collision energies as low as 4 kcal/mole.

Studies of Inelastic and Reactive Collision Dynamics Using High Resolution H atom TOF Spectroscopy

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We have recently assembled a fixed-source, rotatable detector crossed molecular beams apparatus for studies of inelastic and reactive bimolecular collision dynamics. Although our long-term goal is to study elementary reactions relevant to combustion chemistry, we have begun with a relatively simple system in order to evaluate the sensitivity and resolution of the apparatus: H + DCl → HCl + D. Recent theoretical calculations[1] suggest the possible existence of two competing mechanisms: 1) direct Cl abstraction by H with the HCl product "backscattered" relative to the incident H atom, and 2) insertion of the H atom into the DCl bond leading to "sideways" scattered HCl product. Although this reaction has been studied by several groups using a variety of methods, there have been no studies in which both product angular and velocity distributions have been determined.

A fast photolytic beam of H atoms is produced by UV photodissociation of HI. This beam crosses a DCl beam at 90 degrees and the resulting D atom products are detected as a function of scattering angle using the Rydberg tagging method. Current progress on this project will be discussed.

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New Way of Controlling Molecular Processes by Lasers

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It is well known that various molecular dynamic processes can be induced or enhanced by lasers, most of which are governed by nonadiabatic transitions at avoided crossings between the so called dressed (or Floquet) states. Various ideas have been proposed to control molecular processes by manipulating lasers. Here, we propose two new ideas. One is to control nonadiabatic transitions by sweeping the laser frequency $\omega(t)$ periodically at avoided crossings.[1] By appropriately choosing the number and amplitude of the periodic sweeping, we can control the transition as we wish no matter what value the nonadiabatic transition probability takes. The control parameters can be determined analytically with the help of the new semiclassical theory of time-dependent nonadiabatic transition. [2,3] This idea can be further generalized to use also the laser intensity $I(t)$ as an adiabatic parameter to be swept. Sweeping $\omega(t), I(t)$ or both corresponds to the Landau-Zener-Stueckelberg type, the Rosen-Zener-Demkov type, or the exponential potential type nonadiabatic transitions, respectively. Some examples will be shown. The second is to utilize the intriguing phenomenon of complete reflection in the nonadiabatic tunneling type transitions.[3,4] An example of controlling photodissociation will be presented.

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Half-Collision Scattering Dynamics of OH Radicals with *ortho-* and *para*-D_2

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The infrared spectrum and predissociation dynamics of *ortho-* and *para*-D_2-OH in their ground electronic state have been examined by IR-UV action spectroscopy. Infrared excitation at 1.4 μm prepares D_2-OH in well-defined initial states with two quanta of OH stretch and possible intermolecular bending excitation. The OH vibrational excitation provides sufficient energy to surmount the barrier to the OH + D_2 → HOD + D reaction or, alternatively, to break the weak intermolecular bond and regenerate reactants. The OH fragments from vibrational predissociation are monitored with an ultraviolet probe laser on various $A\,^2\Sigma^+$ - $X\,^2\Pi$ transitions. Time-resolved studies show that vibrationally activated D_2-OH (v_{OH}=2) is short-lived (≤ 5 ns). The OH (v=1, j_{OH}) product state distribution reveals that the D_2 partner becomes vibrationally excited as a result of an efficient near-resonant vibration to vibration energy transfer process. A closer look at the OH fragments yields their rotational and fine structure distributions. A surprising Λ-doublet selectivity is observed, which is strongly dependent on the initial state of *ortho-* or *para*-D_2-OH. The OH pπ orbital is preferentially aligned, either perpendicular or parallel to the OH rotation plane, for different states of *para*-D_2-OH and not aligned for *ortho*-D_2-OH. These results are consistent with half-collisions that sample different restricted angular regions of the OH + D_2 potential energy surface for each of the initially prepared states. Quantum calculations of the *ortho-* and *para*-D_2-OH bound states and wave functions will be presented in support of the experimental observations.

Reactions of $N(2^2D)$ with CH_3OH and its Isotopomers

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The reaction pathways of $N(^2D)$ with methanol and its isotopomers were specified by laser pump-and-probe experiments and molecular orbital calculations. It was shown experimentally that CH_3OH deactivates $N(^2D)$ efficiently to produce ground state NH and OH radicals. The nascent state distributions of these radicals are not statistical, suggesting that the intermediate species decompose before energy randomization. A similar result was obtained for ND and OD formed in the $N(^2D)/CD_3OD$ system. NH, ND, OH, and OD radicals were identified in partially deuterated systems. The ND/NH population ratio measurements show that NH and ND radicals are produced from both hydroxyl and methyl positions, but the former plays more important roles, one order of magnitude, than the latter. This is consistent with the result of ab initio molecular orbital calculations that the most favorable initial step is the addition of $N(^2D)$ to the O atom. Since atomic oxygen has an unshared electron pair, the additive $CH_3O(N)H$ complex is stable. During the lifetime, an H atom migrates to produce an insertive CH_3ONH complex, which decomposes to CH_3O+NH or CH_3+HNO. The OD/OH ratio in the CD_3OH system as well as the OH/OD ratio in the CH_3OD system is 0.5. OH(OD) is produced mainly by the C–O bond scission just after the insertion of $N(^2D)$ into a C–H(C–D) bond, but the bond scission after intramolecular H/D scrambling is also important. This is also consistent with the result of calculations that the barrier height for the H(D) atom migration is much lower than the available energy. This H(D) atom migration can be related to the tri-radical character of atomic nitrogen.

Orienting the OH radical

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In recent pulsed crossed molecular beam experiments we have determined the state-to-state cross sections for rotational excitation of OH($X^2\Pi$) radicals [1], and the steric dependence of these cross sections on the orientation of OH, in collisions with various atoms and molecules [2,3].

The OH radicals were formed in an electric discharge at the orifice of the valve. Initial state preparation of the OH beam was achieved by rotational cooling in the expansion, followed by electrostatic hexapole focusing to select one initial Λ-doublet substate. LIF spectroscopy was used to determine the population of the rotational states of OH with and without collisions to determine relative state-to-state cross sections. To measure the steric dependence the OH radicals were oriented by a static electric field at the collision area (the hexapole state selection and orientation technique). By changing the direction of the electric field we were able to perform experiments in which the secondary molecule collides with the H-side or the O-side of the OH molecule, respectively

The steric dependence of the cross sections has been determined for collisions of OH with He, Ar, n-H_2, p-H_2, N_2 and CO. Steric effects up to 70% have been measured in collisions with N_2, indicating the excitation cross section for collisions at the H-side is 5.5 times as large as the cross section for collisions at the O-side. For spin-orbit conserving transitions excitation at the H-side is preferred in transitions to higher rotational states, while for spin-orbit changing transitions no general behavior has been observed.

In this presentation we will discuss the experimental techniques to perform state-to-state collision experiments with oriented OH radicals. We will explain how OH can be oriented and how the orientational probability density function can be probed using a narrow band pulsed dye-laser. The influence of polarization and saturation on population measurements will be discussed, as well as the characterization of the OH production by microwave, cavity-ring-down and 1-dim. LIF spectroscopy.

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Photodissociation of water in the second absorption band:

the complete picture

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In the second absorption band the electronic $\tilde{B}^1A_1$ state, which has a linear equilibrium geometry, is excited. The conical intersection between the $\tilde{B}$ state and the ground state $\tilde{X}^1A_1$ plays an important role in the photofragmentation process. Three dimensional potential energy surfaces for the $\tilde{X}$, $\tilde{B}$ and $\tilde{A}^1B_1$ states, as well as the transition dipole moment between the $\tilde{B}$ and $\tilde{X}$ state, have been calculated accurately using the MRD-CI method. For a correct description of the conical intersection, and at the same time the Renner-Teller coupling between the $\tilde{A}$ and $\tilde{B}$ state, roto-electronic wave functions have been constructed in which $\vec{J_z}\vec{L_z}$ is diagonal, where J_z and L_z are the projection of the total and electronic angular momentum on the z axis, which is parallel to an OH bond. Matrix elements of the electronic angular momentum have been calculated explicitly from the ab initio electronic wave functions. The photodissociation of water in the ro-vibrational ground state ($J = 0$) then proceeds via five coupled roto-electronic states. The effect of the Coriolis interaction was also investigated.

The dynamics was studied using wave packet methods. The calculated absorption spectrum is in good agreement with experiment. The apparently regular absorption spectrum is shown to be composed of overlapping resonances with a complicated structure. The resonant wave functions, which are dominantly located on the adiabatic $\tilde{B}$ surface, have a nodel pattern that corresonds to strongly excited bending motion coupled to OH stretch motion. The $X^2\Pi(OH)/A^2\Sigma^+(OH)$ branching ratio and the vibrational and rotational distribution for X(OH) and A(OH) are in good agreement with experiments. We found significant vibrational excitation for A(OH), but the vibrational distribution for X(OH) is strongly peaked at $\nu=0$, in agreement with recent experiments.

Open Shell Atom-Linear Molecule Interaction and Role of Charge Transfer in the Bond Stabilization*

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Potential energy surfaces may be anticipated through ab-initio calculations or alternatively with semi-empirical methods. The more important test of their reliability is represented by the comparison with those experimentally determined.

Quantum calculations give accurate results for very simple cases but are up to now unable to represent adequately the interactions in the full intermolecular distance range for many electron systems. In the latter case a complete evaluation of the relevant contributions to the interaction and of their relative role is often difficult. Semi-empirical approaches, which blend empirical and theoretical information, besides providing an insight into the nature of relevant interaction components offer perspectives for extension to more complex systems. Furthermore they provide accurate descriptions of the asymptotic behavior of the potential energy surfaces and can be successfully applied to the study of the dynamics of those processes driven by this portion of the interaction.

The interaction of the atom-molecule and ion-molecule systems will be represented as an harmonic expansion, whose moments depend on the intermolecular distance, while the dependence on the mutual orientation of the open shell electronic cloud with respect the molecular axis will be given by spherical harmonics. The identification of the specific physical nature of each radial term of the expansion will lead to their quantitative evaluation through the use of appropriate empirical correlation formulas, some of which are available as discussed above, and some have to be developed. These formulas refer to the anisotropic van der Waals, including dispersion and induction effects, electrostatic and charge transfer components of the interaction. The manifold of the potential energy surfaces will be obtained through an appropriate diagonalization of the interaction matrix including spin-orbit effects. The effectiveness of this approach will be firstly tested on the study of the prototype $F+H_2$ system, for which accurate potential energy surfaces are available also from full quantum calculations.

Application of this approach to the $Cl-H_2$ case and to the ion-molecule system $(Ar-N_2)^+$, where the charge transfer effects are important also for the dynamics, is in progress.

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Unimolecular dissociation of HOCL: Unexpectedly broad distribution of rate constants and underlying wavefunctions

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Abstract

The dissociation of HOCL in its electronic ground state is investigated by means of quantum dynamics calculations (filter diagonalization and harmonic inversion of the autocorrelation function) and an ab initio potential energy surface. Whether a particular resonance state decays slowly or fast ultimately depends on the shape of the underlying wavefunction. We found that at threshold the state-resolved rate constants are scattered over seven orders of magnitude which is significantly broader than the distribution predicted by random matrix theory. We try to rationalize this unexpectedly broad distribution of resonance widths in terms of the nature of the wave functions near the HO+Cl threshold. We will focus the discussion on (i) how the level pattern and the underlying wave functions change with energy from the bottom of the potential well to the HO+Cl dissociation threshold and above, (ii) how new states more or less suddenly appear as a consequence of a saddle node bifurcation of the classical phase space, and (iii) how the structure of the bound state spectrum affects the state specific dissociation rates.

Reaction Dynamics of Neutral Transition Metal Atoms with Unsaturated Hydrocarbons

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The reactions of ground state neutral transition metal atoms (M=Y,Zr,Nb) with unsaturated hydrocarbons such as ethylene (C_2H_4) or acetylene (C_2H_2) usually involves initial formation of π-bonded addition complexes (*e.g.* MC_2H_2). Such complexes may decay back to the M + C_2H_2 reactants (inelastic scattering) or undergo C-H bond insertion leading to HMC_2H. Unimolecular reactions of such intermediates may proceed via several competing channels such as hydrogen atom loss (forming MC_2H + H) or molecular hydrogen elimination (forming MC_2 + H_2).

We have constructed a rotatable source crossed molecular beams apparatus in order to study these reactions under well-defined single collision conditions. The velocity distributions of the neutral chemical products and inelastically scattered reactants are detected as a function of scattering angle using electron impact ionization or 157 nm photoionization mass spectrometry. Studies of the competing channels as a function of collision energy provides insight into a number of important features of the potential energy surfaces for transition metal-hydrocarbon interactions. For example, the heights of potential energy barriers for C-H insertion and the existence of exit channel barriers for unimolecular decomposition leading to final products have been determined from our experimental studies. In some cases, fundamental thermochemical quantities such as M-C bond strengths in simple neutral complexes may also be derived.

Very Long Range Electronic Energy Transfer in the Gas Phase: CO($A^1\Pi$) + pyrazine(S_0) --> CO($X^1\Sigma$) + pyrazine(3R)

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Electronic energy transfer in condensed media has been extensively studied in systems as varied as the light harvesting chromophores of plant cells and metallic ions in solid state lasers. Gas phase studies have been rare. Forster put forth a dipole-dipole mechanism with the crucial factor being the overlap of the donor emission spectrum with the acceptor absorption spectrum. Below is the part of the absorption spectrum of pyrazine which overlaps the A-X emission of CO. The latter is represented by a series of bars representing the relative intensities of the (0,v") transitions (v"=0,1,2,3,4)
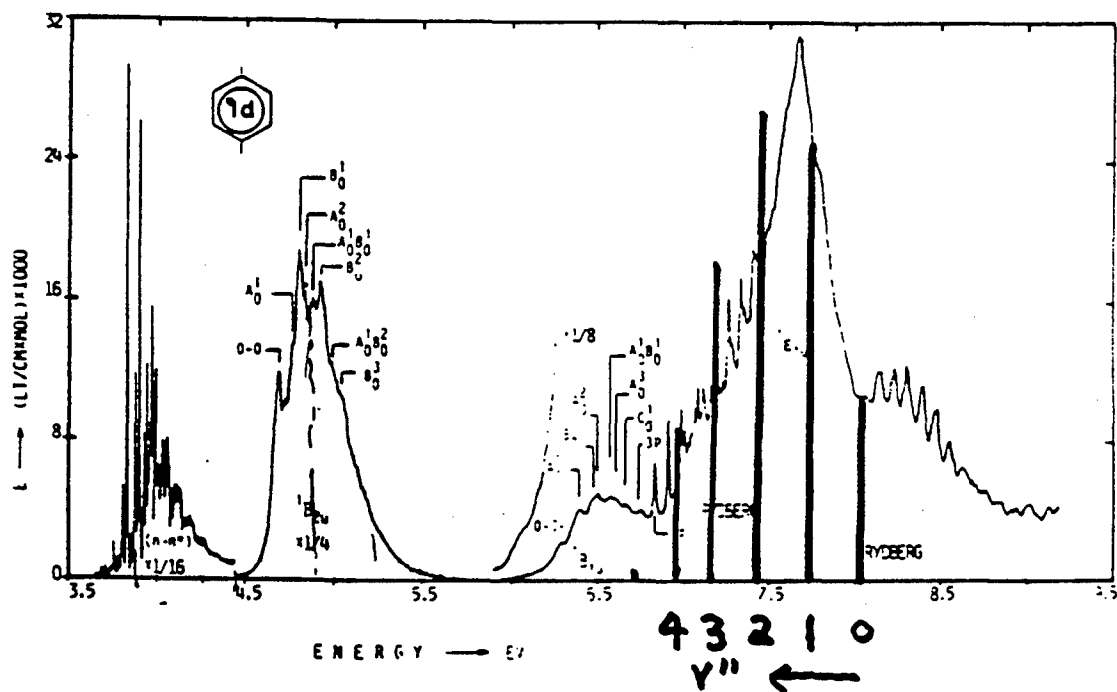
The fluorescence intensity of 30 millitorr of CO excited by a vuv laser at 154 nm (8.05 eV) was measured as a function of pyrazine pressure from 7 to 22 millitorr at which pressure it was almost totally quenched. There was no significant (outside the statistical error) variation of the quenching cross section with the initial J state of the CO. An enormous cross section averaged over 11 rotational states of 17300 ± 3900 A^2 was measured. This in turn was due to the intense absorption of pyrazine ($e_{max} = 30,000$) in the region overlapping the CO emission. The theoretical interest of the present result is that with such a large cross section a) the overlap of the donor and acceptor charge distributions plays no role and b) the dipole-dipole approximation is truly valid.

Ion Imaging and Wave Packet Studies of the Photodissociation Dynamics of IBr.

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The visible and UV spectroscopy as well as photochemistry of diatomic inter-halogens (such as BrCl, Br_2, or IBr) is highly complex as a large number of excited electronic states are involved. In particular IBr has attracted special interest, because the avoided crossing between its $B(^3\Pi_{0+})$ and $B'(0^+)$ excited states is of *intermediate* strength, *i.e.* neither an adiabatic nor diabatic picture of these states is suitable. Whereas recent femtosecond pump-probe experiments and corresponding wave packet calculations concentrate on the nonadiabatic dynamics of the avoided crossing the aim of this work is an overall picture of the IBr photolysis including all the excited states accessible with a single photon in the visible and near-UV wavelength region.

Experimentally, the photofragment ion imaging technique was used to investigate IBr photolysis in the wavelength range from 600 nm down to 267 nm. Angular and velocity distributions of both the Br and I fragments either in their $X(^2P_{3/2})$ ground or $X^*(^2P_{1/2})$ spin-orbit excited state were measured. The extracted anisotropy parameters β and branching fractions $X^*/(X+X^*)$ provide quantitative information about the excitation to and the nonadiabatic couplings between the different states involved in the photolysis process.

In order to describe the photodissociation dynamics theoretically, wave packet calculations have just been carried out on the multiple, coupled potentials, the results of which will be presented at the conference for comparision with the experiment. It turns out that the IBr potential curves are not well known in particular in the unbound region of interest for this study. Fortunately, the additional experimental information available from the ion imaging study could be used to improve the repulsive walls of the low lying excited states.

On the role of conical intersections in internal conversion

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The role of conical intersections in the internal conversion $S_1 \rightarrow S_0$ of photoexcited H_2CCO and NHCO is considered. The energy minimized portion of the S_1 - S_0 seam of conical intersection near the minimum energy crossing point is studied as a function of key internal coordinates. The characteristic parameters of the conical intersection points are used to: identify the two modes that evince the conical nature of the intersection; determine the energy and singular part of the derivative coupling near the conical intersection; and construct a transformation to diabatic states that rigorously removes the singularity in the derivative coupling. For ketene barrierless paths on S_1 from the Franck-Condon region of the $S_0 \rightarrow S_1$ excitation, leading to $\mathbf{R}_e(A^1A'')$, the equilibrium geometry of S_1 ketene, and to $\mathbf{R}_{mex}$, the minimum energy point on the $S_1- S_0$ seam of conical intersection, were identified. The mechanistic implications of these results are discussed. If sufficient progress is made the quenching of OH(A) by H_2 will also be discussed.

A Spectral Transform Krylov Subspace Iteration Approach to Quantum Scattering

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A spectral transform Lanczos iteration method is suggested for finding the eigenvalues and eigenvectors of the coupling matrix appearing in quantum scattering calculations. Three main attributes which makes the implementation highly efficient are:

- Partial reorthogonalization of the Lanczos vectors.

- Guided spectral transform filter.

- DVR basis.

The method was first used to perform 3D rotating line umbrella (RLU) calculations of the reaction $Cl+CH_4 \rightleftharpoons HCl+CH_3$, where it was shown that it is substantially faster than the direct diagonalization method. Calculated state-to-state reaction probabilities as well as adiabats agree with previous results obtained using direct diagonalization of the coupling matrix. In the RLU model the two reactive bonds and the umbrella motion are explicitly treated quantum dynamically.

We have recently developed a dual-level ab initio analytic potential energy surface for the RLU treatment of $Cl+CH_4$ with a classical barrier height of 6.96 kcal/mol for the forward reaction and 5.40 kcal/mol for its reverse. This surface, with zero point energy corrections for the modes not treated explicitly, has been used to study the $Cl+CH_4 \rightleftharpoons HCl+CH_3$ and $Cl+CD_4 \rightleftharpoons DCl+CD_3$ reactions. Large isotope effects were found, in good agreement with experimental results.

We have developed a 4D rotating bond umbrella (RBU) approach and, using the spectral transform Lanczos iteration method, applied it to the $Cl+CH_4 \rightleftharpoons HCl+CH_3$ and $H+CH_4 \rightleftharpoons H_2+CH_3$ reactions. In these calculations the reactive bonds, the umbrella motion and a CH_4 bending vibration, which correlates to CH_3 rotation, are treated explicitly.

Using reduced dimensionality models, treating from 2 to 4 dimensions explicitly, we have calculated several experimentally measured quantitites like thermal rate constants and state-to-state differential and integral cross sections and found good overall agreement. However, for the reaction of $Cl+CH_4$ with one quantum of energy in the ν_3 mode we obtain the methyl radical significantly excited in the umbrella mode, which does not agree with the experimental results. This may be due to geometrical restrictions in the reduced dimensionality models.

Theoretical studies on the 'One atom cage effect' in Van der Waals complexes

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When a molecule dissociates in a solvent, the separation of the photofragments can be inhibited by the surrounding atoms or molecules, which act as a cage. This effect has also been observed in Van der Waals complexes where a molecule is complexed by only one rare gas atom, which plays the role of the 'cage'. This is the so-called 'one atom cage effect'.

Using wave packet propagation techniques, we have studied this effect in $I_2 \cdots$ Ar interacting with ultrashort laserpulses, which allow for a real-time detection of the breaking of molecular bonds or nuclear vibrations. Two cases of the 'one atom cage' effect in $I_2 \cdots$ Ar are considered:

The first concerns the photodissociation and recombination of I_2 in the presence of rare gas atoms at high pressures. The dynamics of the dissociation and recombination is studied by simulations of short pulse excitation and wave packet propagations [1]. The results will be compared to recent pump-probe experiments performed in the group of A. Zewail [2].

In the second example we consider the photodissociation of the $I_2 \cdots$ Ar Van der Waals complex with ultrashort laserpulses. Based on recent *ab-initio* potentials [3], we compare results of wave packet calculations [4] with experimental results on the 'one atom cage effect' [5]. The excellent agreement allows for a clear interpretation of this effect. Furthermore, the effects of pulse duration and chirped laserpulses are investigated.

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Crossed Molecular Beam Studies of Rotationally Inelastic Collisions

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The first images of quantum-state-selected scattering from a new crossed molecular-beam machine have been obtained and analyzed. A complete data set has been obtained for the rotationally inelastic collisions

$$HCl \ (J=0) + Ar \rightarrow HCl \ (J'=0\text{-}6) + Ar.$$
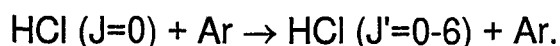
HCl is seeded in a supersonic expansion of Ar and crossed at 90° with another supersonic expansion of neat Ar. Resonantly enhanced multiphoton ionization of the HCl through the E state is used in order to state-selectively ionize the HCl produced by rotationally inelastic collisions. The product ions are projected onto a position sensitive ion detector using electrostatic lenses with voltages such that the ions are velocity mapped onto the detector. In this way we obtain an image that can be analyzed to extract a differential cross section for the scattering event.

The experimental differential cross sections are compared directly with calculated differential cross sections generated using Jeremy Hutson's Ar-HCl potential and MOLSCAT program. Data sets for several other systems have been taken: CO/He, CO/Ne, NO/D_2, NO/He and HCl/Kr. These systems were chosen due to the availability of good potential energy surfaces for comparison, the ability to perform state-selected REMPI on the collision partner, and these collision partners represent prototype inelastic scattering systems. HCl has a large dipole, CO has a small dipole and NO has two nearly degenerate lambda doublets states (as do all radical species) for scattering.

Quenching highly excited molecules: the fire extinguisher or the fire · hose?

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The collisional relaxation of highly excited molecules is explored using high-resolution transient IR absorption techniques. Highly excited molecules are prepared with well-defined initial energies using pulsed tunable UV excitation (λ=250-330 nm), followed by rapid radiationless decay to ground electronic state. Collisions that remove energy from the hot molecules are investigated by monitoring the energy gain in neighboring bath molecules using IR diode and f-center lasers. Nascent rotational and translational energy gain distributions of the bath measured at short times following UV excitation provide information about energy partitioning in single-collision relaxation processes. Energy-dependent studies[1] provide independent measurements of energy transfer magnitudes and probabilities and reveal important information regarding the dynamics of supercollision relaxation, including the functional form of the high energy tail of $P(E,E')$. The influence of donor polarity is explored by comparing the relaxation of excited pyridine (μ=2.2 D)[2] with that of excited non-polar pyrazine.[3] A comparison of energy gain pathways for CO_2 and water[4] highlight the role of molecular structure, mass and intermolecular forces in the collisional relaxation dynamics.

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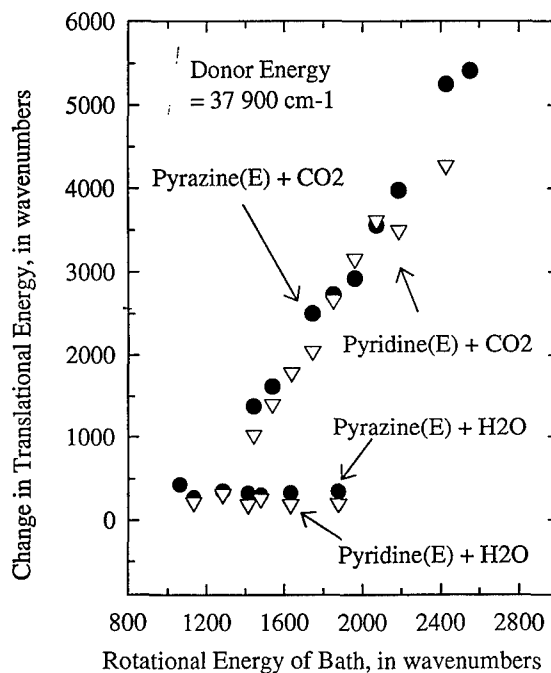
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